Electronic Supplementary Information (ESI)

Cyclopolymerization: A versatile approach to multicyclic polystyrene and polystyrene-containing multicyclic copolymer

Yamato Ebii, [a] *Yoshinobu Mato,* [b] *Feng Li,* [b] *Kenji Tajima,* [b] *Takuya Yamamoto,* [b] *Takuya Isono* *[b] *and Toshifumi Satoh* *[b]

[a]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan

[b]Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

E-mail: isono.t@eng.hokudai.ac.jp
satoh@eng.hokudai.ac.jp

Table of Contents

S1. Materials

Grubbs' catalyst 3rd generation (G3) was prepared according to previously reported method.[1] *N*,*N*-Dimethyl-4-aminopyridine (DMAP; Tokyo Chemical Industry Co., Ltd. (TCI), >99.0%), 1-ethyl-3-(3-(dimethylamino)-propyl)carbodiimide hydrochloride (EDC; TCI, >98.0%), ethyl vinyl ether (TCI, >98.0%), (±)-*exo*-5-norbornenecarboxylic acid (*exo*-NB-COOH; Aldrich, 97%), *rac*-lactide (LA; TCI, >98.0%), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU; TCI, >98.0%), 1-butanol (Wako Pure Chemical Industry Co. Ltd., >99.0%), CH_2Cl_2 (Junsei Chemical Co., Ltd., >99.0%), methanol (Aldrich, >99.8, dry methanol (Kanto Chemical Co., Inc., >99.5%), *sec*-butyllithium (*sec*-BuLi; Kanto Chemical Co., Inc., 1.23 mol L^{-1} in cyclohexane/*n*-hexane (v/v = 24/1)), and dry CH_2Cl_2 (Kanto Chemical Co., Inc., >99.5%, water content, <0.001%) were used as received. HO–PS–OH samples were obtained from Polymer Source and used as received. Styrene (TCI, >99%), propylene oxide (PO; TCI, >99.0%), and cyclohexane (Kanto Chemical Co., Inc., >99.5%) were purified by distillation over CaH_2 under reduced pressure. Linier polystyrenes synthesized by anionic polymerization with *sec*-BuLi as an initiator were obtained from Shodex and used as received.

S2. Instruments

The polymerization experiments were carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, O_2<0.1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 moisture sensor and an MB-OX-SE 1 oxygen sensor, respectively. The ^{1}H (400 MHz) spectra were recorded using a JEOL JNM-ECS400 instrument at room temperature in $CDCl_3$. The size exclusion chromatography (SEC) was performed at 40 °C in THF (flow rate, 1.0 mL min^{-1}) using a Shodex GPC-101 gel permeation chromatography system (Shodex DU-2130 dual pump, Shodex RI-71-S reflective index detector, and Shodex ERC-3125SN degasser) equipped with a Shodex KF-G guard column (4.6 mm × 10 mm; particle size, 8 μm) and two Shodex KF-804L columns (linear, 8 mm × 300 mm) or Jasco high-performance liquid chromatography system (PU-3 980 Intelligent HPLC Pump, CO-2065 Plus Intelligent Column Oven, RI-2031 Plus Intelligent RI Detector, and DG-2080-53 Degasser) equipped with a Shodex KF-G guard column (4.6 mm × 10 mm; particle size, 8 μm) and two Shodex KF-804L columns (linear; particle size 7 μm; 8.0 mm × 300 mm; exclusion limit, 4×10^4) or Jasco high-performance liquid chromatography system (PU-4180 HPLC pump, AS-4550 auto sampler, and CO-4060 column oven) equipped with a Shodex K-800D guard column (8.0 mm × 100 mm; particle size, 10 μm), two Shodex columns (K-806L and K-804L; linear, 8.0 mm × 100 mm; particle size, 10μm) (which was only used for the measurement of NB–PS_{52k}–NB and *mc*-PS_{52k}) . The absolute number-averaged molecular weight ($M_{n,MALS}$) and polydispersity ($Đ_{MALS}$) of the samples were determined by SEC with multiangle light scattering detection (SEC-MALS-Visco) in $CHCl_3$ (flow rate, 1.0 mL min^{-1}) at 40 °C using a Jasco high-performance liquid chromatography system (PU-4180 HPLC pump, AS-4550 auto sampler, and CO-4060 column oven) equipped with a Shodex K-800D guard column (8.0 mm × 100 mm; particle size, 10 μm), two Shodex columns (K-806L and K-804L; linear, 8.0 mm × 100 mm; particle size, 10μm), a DAWN 8 multiangle laser light scattering detector (Wyatt Technology), a Viscostar viscosity detector (Wyatt Technology), and an RI-501 refractive index detector (Shodex). The preparative GPC was performed at room temperature in $CHCl_3$ (flow rate, 10.0 mL min^{-1}) using LaboACE LC-7080 liquid chromatography system (Japan Analytical Industry Co. Ltd.) equipped with a P-LA80 pump, a RI-700LA RI detector, JAIGEL-HR-P guard column (8 mm × 40 mm; Japan Analytical Industry Co. Ltd.), JAIGEL-2HR column (linear, 20.0 mm × 600 mm; exclusion limit, 5.0×10^3), JAIGEL-2.5HR column (linear, 20.0 mm × 600 mm; exclusion limit, 2.0×10^4), and JAIGEL-3HR column (linear, 20.0 mm × 600 mm; exclusion limit, 7.0×10^4).

Differential scanning calorimetry (DSC) measurement

The DSC experiments were performed using a Hitachi DSC 7000X under a nitrogen atmosphere. The samples of *mc*-PS were heated to 150 °C, cooled to 30 °C, and heated again to 150 °C at the heating and cooling rate of 10 °C min^{-1} and 20 °C min^{-1}, respectively. The samples of PS-containing multicyclic copolymers were heated to 150 °C, cooled to −10 °C, and heated again to 150 °C at the heating and cooling rate of 10 °C min^{-1} and 20 °C min^{-1}, respectively.

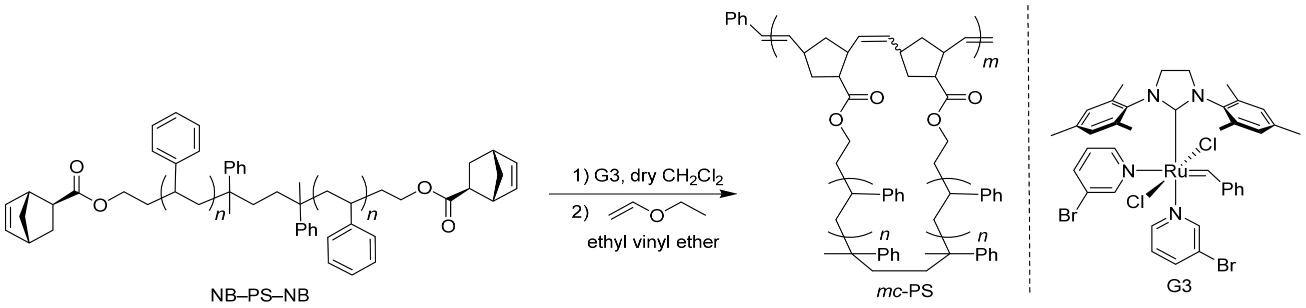
Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS)

The MALDI-TOF MS measurement of the obtained products was performed using an Bruker Daltonics (Germany) Ultraflex MALDI-TOF/TOF mass spectrometer equipped with a 355-nm Nd:YAG laser. PS samples were prepared by depositing a mixture of the polymer, matrix, and cationic agent in THF onto a sample plate. A 10:10:1 (v/v) ratio of [PS (1 g L^{-1} in THF)]/[*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-propenylidene]malononitrile (DCTB; 20 g L^{-1} in THF)]/[silver trifluoroacetate (2.0 g L^{-1} in THF)] was used.

S3. Synthetic details and additional dates

Synthesis of *mc*-PS

Scheme S1. Synthesis of *mc*-PS



A typical procedure for the ring-opening metathesis polymerization (ROMP) is as follows (Method B): In a three-necked flask, a stock solution of Grubbs third-generation catalyst (G3; 2.54 mL, 20.3 μmol as a 8.0 mol L^{-1} in dry CH_2Cl_2, 1.0 eq.) was quickly added to a stirred mixture of *α*,*ω*-dinorbornenyl-functionalized linear polystyrene ($NB–PS_{1k}–NB$; $M_{n,NMR}$ = 1,640, 100 mg, 61.0 μmol, 3.0 eq.) in dry CH_2Cl_2 (122 mL) under an argon atmosphere. After 10 min, an excess amount of ethyl vinyl ether was added to the reacting mixture to terminate the ROMP. The crude product was purified by preparative GPC to remove the catalyst residue, affording *mc*-PS_{1k} as a brown solid. Yield: 82.0 mg (82.0%)

$M_{n,SEC}$ = 3,870, $Đ$ = 1.28, $M_{n,MALS}$ = 5,300, $Đ_{MALS}$ = 1.22, average number of cyclic units = 3.2

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.23–6.12 (m, *aromatic*), 5.79–4.78 (br, alkenyl of poly(norbornene) backbone), 4.31–2.35 (br, alkenyl of poly(norbornene) backbone), 2.44–1.69 (m, –$CH_2C\mathit{H}Ph$–), 1.69–0.99 (m, –$C\mathit{H}_2CHPh$–, –$CH_2CC\mathit{H}_3(Ph)$–, –$C\mathit{H}_2CCH_3(Ph)$–, –$C\mathit{H}_2CH_2OCO$–)

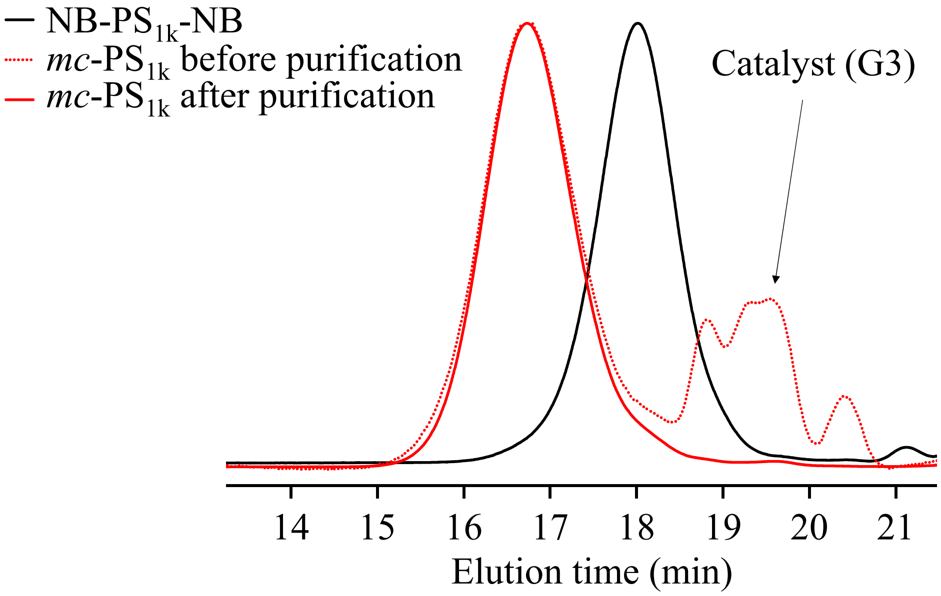
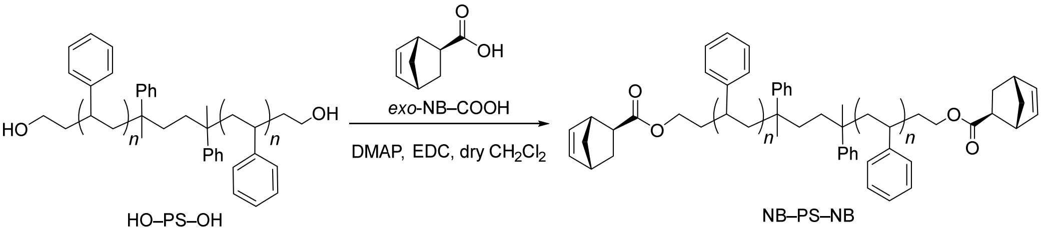


Figure S1. SEC traces of NB–PS_{1k}–NB and *mc*-PS_{1k} obtained from run 1 in **Table 2** before and after purification by preparative GPC (refractive index (RI) detection; eluent, THF; flow rate, 1.0 mL min^{-1}).

Synthesis of *α*, *ω*-end norbornenyl-functionalized PS (NB–PS$_{1k}$–NB)

Scheme S2. Synthesis of NB–PS–NB



A typical procedure for the condensation reaction is as follows (Method A): In a round-bottom flask, HO–PS$_{1k}$–OH ($M_{n,NMR}$ = 1,100, 2.00 g, 1.82 mmol), *exo*-NB–COOH (1.02 g, 7.38 mmol), EDC (2.11 g, 11.0 mmol) and DMAP (1.33 mg, 10.9 mmol) were dissolved in CH$_2$Cl$_2$ (25.0 mL), and the mixture was stirred at r.t. for 96 h. The polymer crude was purified by silica gel column chromatography (CH$_2$Cl$_2$/Methanol = 19/1 (v/v), R_f = 0.29) to give NB–PS$_{1k}$–NB as a white solid. Note that higher molecular weight NB–PS$_x$–PS (x = 6k, 12k, 13k, and 52k) were purified by the reprecipitation from the CH$_2$Cl$_2$ solution into methanol.

Yield: 1.58 g (79.0%)

$M_{n,NMR}$ = 1,640, $M_{n,SEC}$ = 1,220, $Đ$ = 1.55

^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.40–6.17 (m, *aromatic*), 6.18–6.00 (m, 4H, –C*H*=C*H*– in norbornene ring), 3.93–3.60 (m, 4H, –CH$_2$C*H*$_2$OCO–), 3.14–2.91 (m, 4H, –C*H*–CH$_2$–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 2.53–1.69 (m, –CH$_2$C*H*Ph–, *endo*-C*H*– of –CH–CH$_2$–CH–C*H*CO– in norbornene ring, *exo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring), 1.69–1.13 (m, –C*H*$_2$CHPh–, –CH$_2$CC*H*$_3$(Ph)–, –C*H*$_2$CCH$_3$(Ph)–, –C*H*$_2$CH$_2$OCO–, *endo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring, bridge head –C*H*$_2$– in norbornene ring).

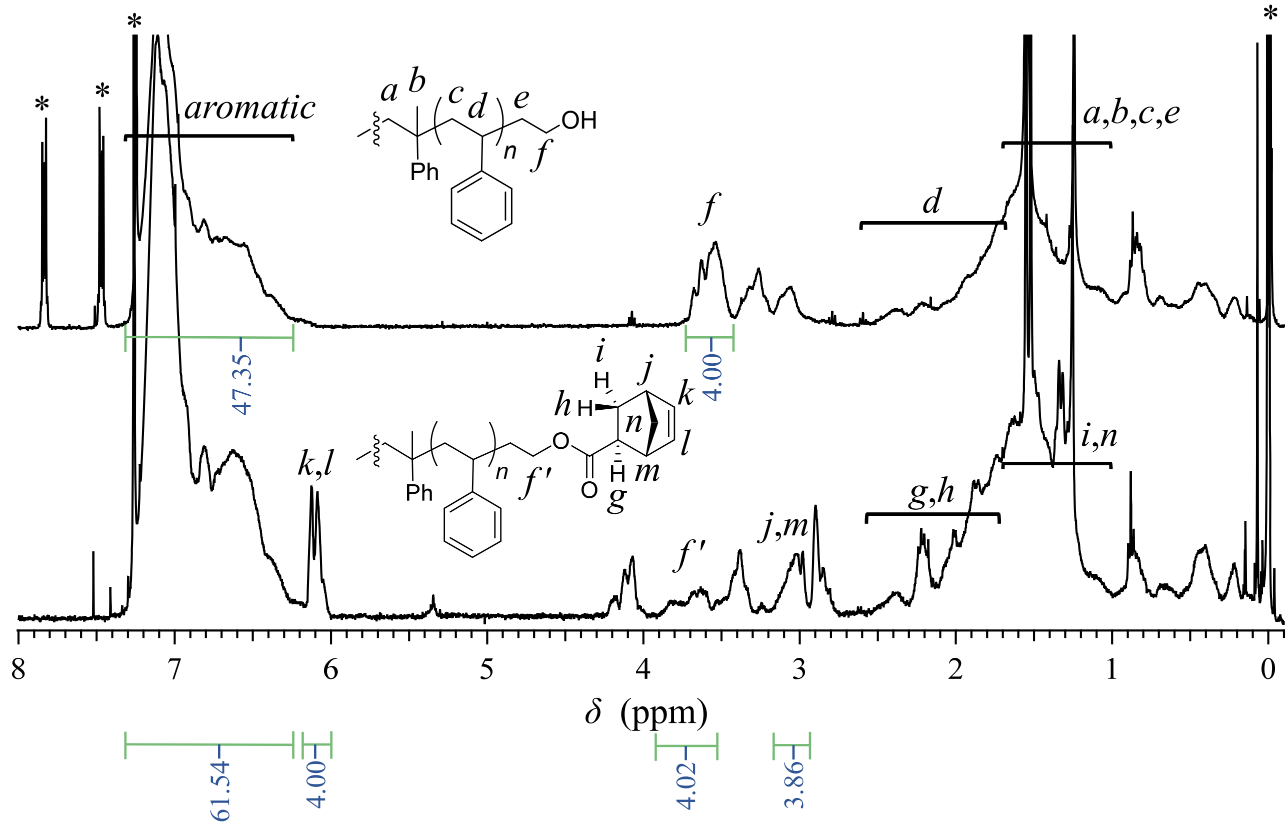


Figure S2. ^{1}H NMR spectra of HO–PS$_{1k}$–OH (upper) and NB–PS$_{1k}$–NB (lower) in CDCl$_3$.

Synthesis of NB–PS_{6k}–NB

Method A was used for the reaction of HO–PS_{6k}–OH ($M_{n,NMR}$ = 6,000, 2.50 g, 417 μmol) with *exo*-NB-COOH (231 mg, 1.67 mmol), DMAP (485 mg, 2.53 mmol), and EDC (485 mg, 2.53 mmol) in CH_2Cl_2 (25.0 mL) for 91 h to give NB–PS_{6k}–NB as a white solid. Yield: 2.45 g (98.0%)

$M_{n,NMR}$ = 6,000, $M_{n,SEC}$ = 5,800, $Đ$ = 1.09, $M_{n,MALS}$ = 6,470, $Đ_{MALS}$ = 1.04

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38–6.17 (m, *aromatic*), 6.17–6.01 (m, 4H, –C*H*=C*H*– in norbornene ring), 3.93–3.62 (m, 4H, $–CH_2CH_2OCO–$), 2.95–2.78 (m, 4H, –C*H*–CH_2–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 2.44–1.69 (m, $–CH_2CHPh–$, *endo*-C*H*– of –CH–CH_2–CH–C*H*CO– in norbornene ring, *exo*-C*H*– of –CH–CH_2–CH–CO– in norbornene ring), 1.69–1.13 (m, $–CH_2CHPh–$, $–CH_2CCH_3(Ph)–$, $–CH_2CCH_3(Ph)–$, $–CH_2CH_2OCO–$, *endo*-C*H*– of –CH–CH_2–CH–CO– in norbornene ring, bridge head $–CH_2–$ in norbornene ring).

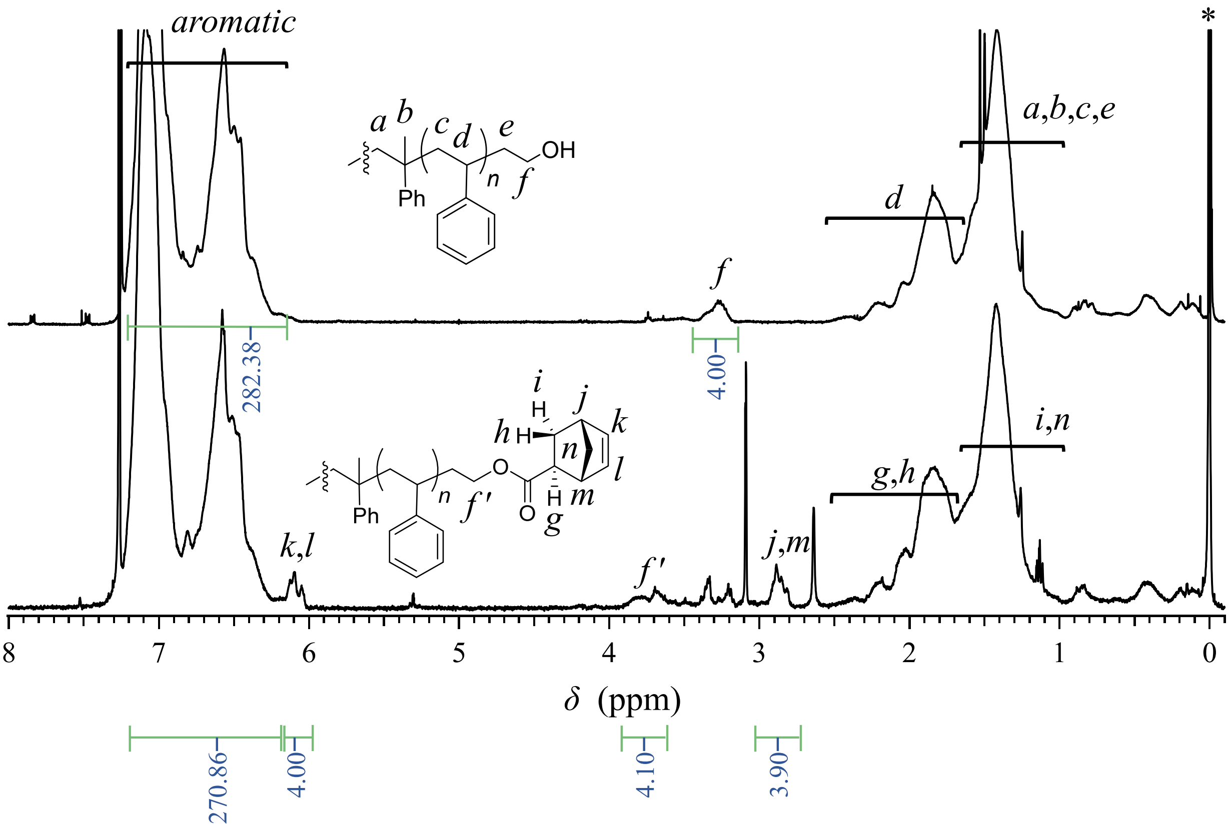


Figure S3. ^{1}H NMR spectra of HO–PS$_{6k}$–OH (upper) and NB–PS$_{6k}$–NB (lower) in CDCl$_3$.

Synthesis of NB–PS$_{12k}$–NB

Method A was used for the reaction of HO–PS$_{12k}$–OH ($M_{n,NMR}$ = 12,000, 2.50 g, 208 µmol) with *exo*-NB-COOH (111 mg, 803 µmol), DMAP (148 mg, 1.21 mol), and EDC (232 mg, 1.21 mol) in CH_2Cl_2 (25.0 mL) for 72 h to give NB–PS$_{12k}$–NB as a white solid. Yield: 1.99 g (79.6%)

$M_{n,NMR}$ = 11,600, $M_{n,SEC}$ = 11,500, $Đ$ = 1.07, $M_{n,MALS}$ = 12,300, $Đ_{MALS}$ = 1.05

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38–6.19 (m, *aromatic*), 6.19–5.96 (m, 4H, –C*H*=C*H*– in norbornene ring), 3.93–3.62 (m, 4H, $–CH_2CH_2OCO–$), 2.97–2.72 (m, 4H, –C*H*–CH_2–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 2.44–1.69 (m, $–CH_2CHPh–$, *endo*-C*H*– of –CH–CH_2–CH–C*H*CO– in norbornene ring, *exo*-C*H*– of –CH–CH_2–CH–CO– in norbornene ring), 1.69–1.13 (m, $–CH_2CHPh–$, $–CH_2CCH_3(Ph)–$, $–CH_2CCH_3(Ph)–$, $–CH_2CH_2OCO–$, *endo*-C*H*– of –CH–CH_2–CH–CO– in norbornene ring, bridge head –CH_2– in norbornene ring).

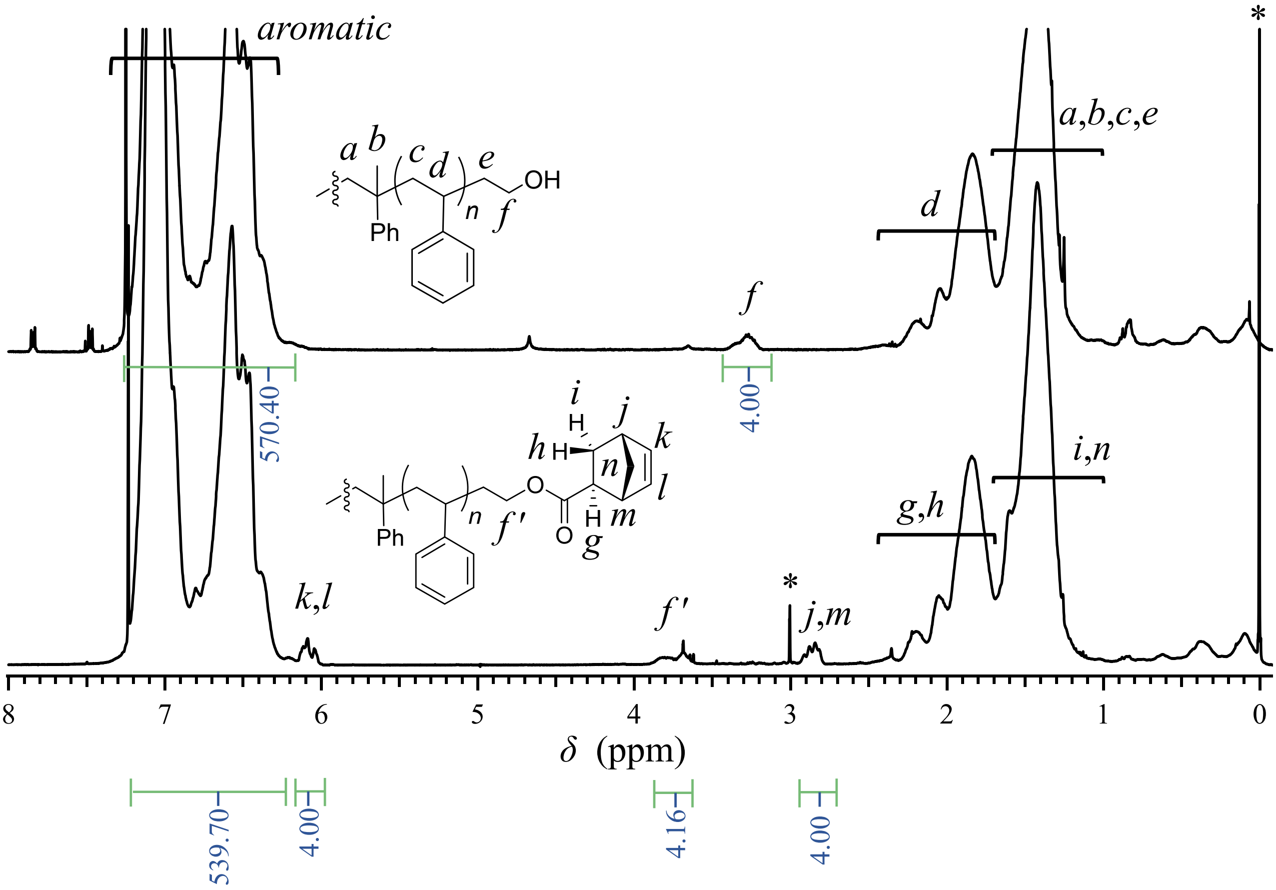


Figure S4. ^{1}H NMR spectra of HO–PS$_{12k}$–OH (upper) and NB–PS$_{12k}$–NB (lower) in $CDCl_3$.

Synthesis of NB–PS_{13k}–NB

Method A was used for the reaction of HO–PS_{13k}–OH ($M_{n,NMR}$ = 11,600, 2.50 g, 216 μmol) with *exo*-NB-COOH (136 mg, 984 μmol), DMAP (181 mg, 1.48 mol), and EDC (284 mg, 1.48 mol) in CH_2Cl_2 (25.0 mL) for 72 h to give NB–PS_{13k}–NB as a white solid. Yield: 2.24 g (89.6%)

$M_{n,NMR}$ = 12,300, $M_{n,SEC}$ = 12,500, $Đ$ = 1.22, $M_{n,MALS}$ = 13,400, $Đ_{MALS}$ = 1.19

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38–6.25 (m, *aromatic*), 6.20–5.98 (m, 4H, –CH=CH– in norbornene ring), 3.92–3.61 (m, 4H, –CH_2CH_2OCO–), 2.96–2.76 (m, 4H, –CH–CH_2–CH–CO– in norbornene ring, –CH–CH–CO– in norbornene ring), 2.44–1.69 (m, –CH_2CHPh–, *endo*-CH– of –CH–CH_2–CH–CHCO– in norbornene ring, *exo*-CH– of –CH–CH_2–CH–CO– in norbornene ring), 1.69–1.16 (m, –CH_2CHPh–, –CH_2CCH_3(Ph)–, –CH_2CCH_3(Ph)–, –CH_2CH_2OCO–, *endo*-CH– of –CH–CH_2–CH–CO– in norbornene ring, bridge head –CH_2– in norbornene ring).

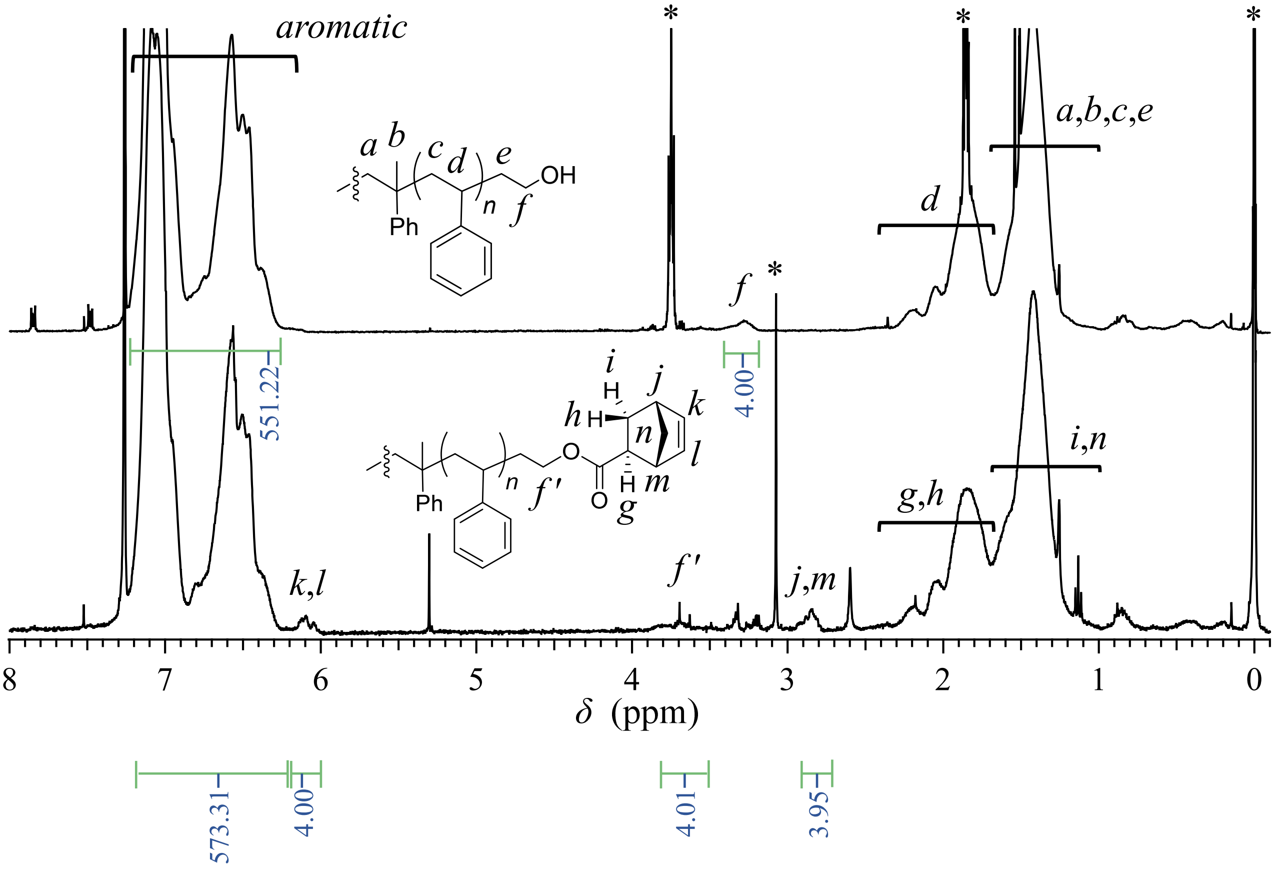


Figure S5. ^{1}H NMR spectra of HO–PS$_{13k}$–OH (upper) and NB–PS$_{13k}$–NB (lower) in CDCl$_3$.

Synthesis of NB–PS_{52k}–NB

Method A was used for the reaction of HO–PS_{52k}–OH ($M_{n,NMR}$ = 55,600, 1.00 g, 17.8 μmol) with *exo*-NB-COOH (15.3 mg, 111 μmol), DMAP (20.3 mg, 166 μmol), and EDC (32.1 mg, 167 μmol) in CH_2Cl_2 (10.0 mL) for 168 h to give NB–PS_{52k}–NB as a white solid. Yield: 837 mg (83.7%)

$M_{n,NMR}$ = 55,600, $M_{n,SEC}$ = 54,400, $Đ$ = 1.06, $M_{n,MALS}$ = 52,100, $Đ_{MALS}$ = 1.01

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.52–6.15 (m, *aromatic*), 6.15–6.00 (m, 4H, –C*H*=C*H*– in norbornene ring), 3.90–3.54 (m, 4H, –$CH_2C\mathit{H}_2$OCO–), 2.94–2.83 (m, 4H, –C*H*–CH_2–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 2.48–1.66 (m, –CH_2C*H*Ph–, *endo*-C*H*– of –CH–CH_2–CH–C*H*CO– in norbornene ring, *exo*-C*H*– of –CH–$C\mathit{H}_2$–CH–CO– in norbornene ring), 1.66–1.15 (m, –$C\mathit{H}_2$CHPh–, –$CH_2CC\mathit{H}_3$(Ph)–, –$C\mathit{H}_2CCH_3$(Ph)–, –$C\mathit{H}_2CH_2$OCO–, *endo*-C*H*– of –CH–$C\mathit{H}_2$–CH–CO– in norbornene ring, bridge head –$C\mathit{H}_2$– in norbornene ring).

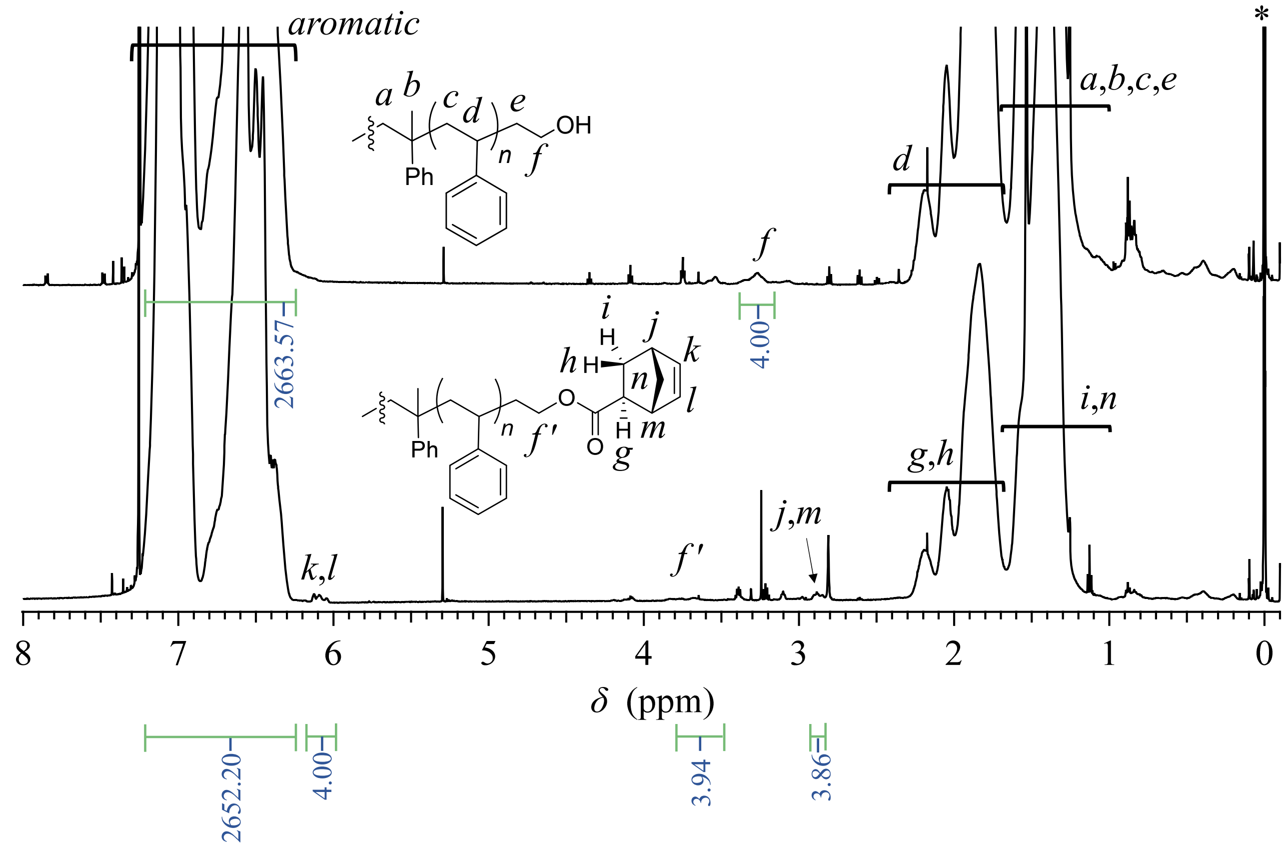


Figure S6. ^{1}H NMR spectra of HO–PS$_{52k}$–OH (upper) and NB–PS$_{52k}$–NB (lower) in CDCl$_3$.

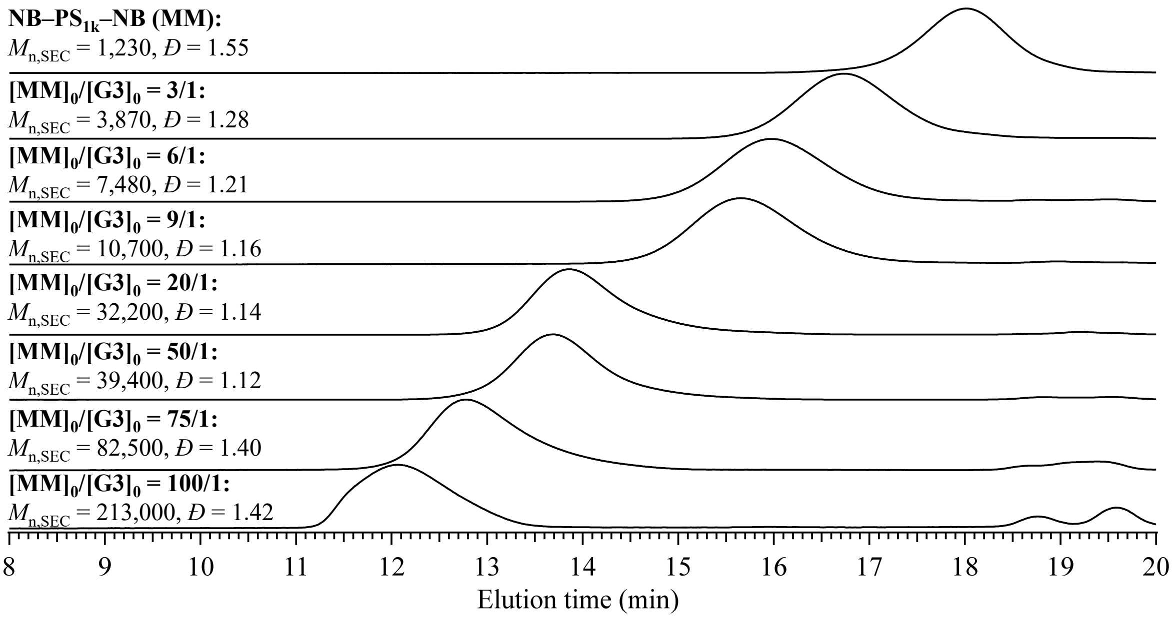


Figure S7. SEC traces of NB–PS1k–NB and *mc*-PS1k obtained from cyclopolymerization (refractive index (RI) detection; eluent, THF; flow rate, 1.0 mL min^{-1}).

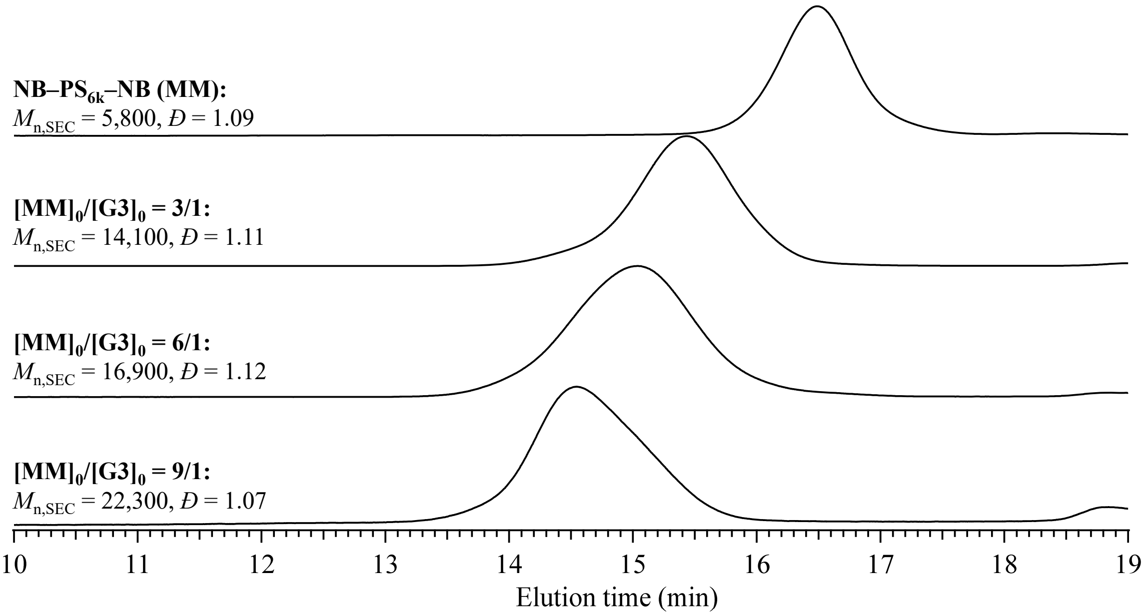


Figure S8. SEC traces of NB–PS6k–NB and *mc*-PS6k obtained from cyclopolymerization (refractive index (RI) detection; eluent, THF; flow rate, 1.0 mL min^{-1}).

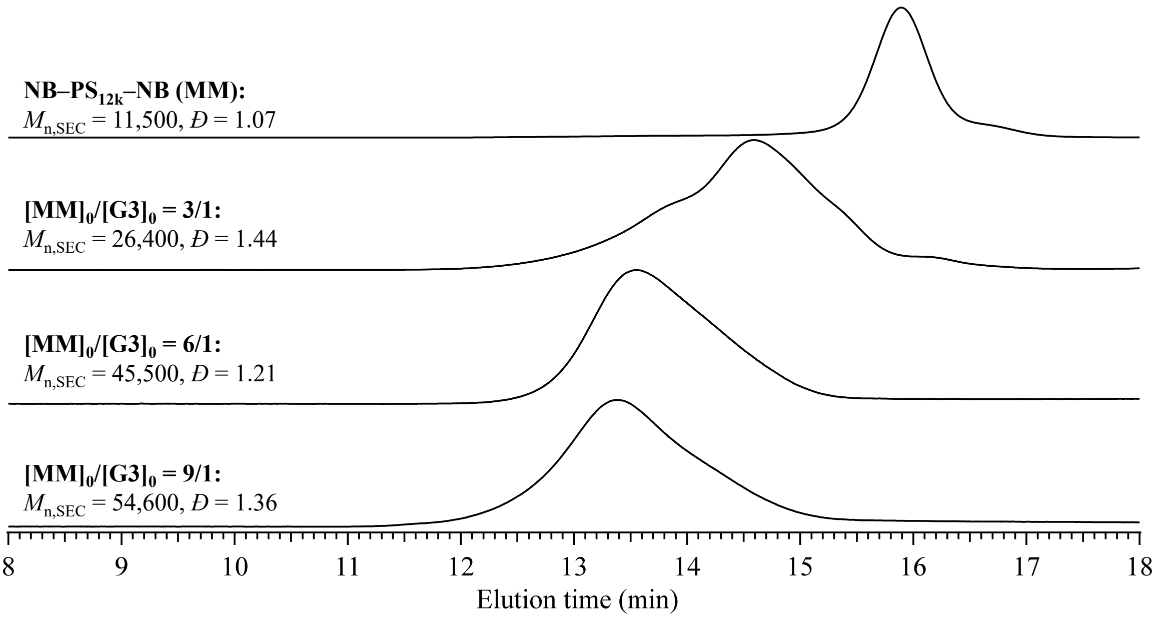


Figure S9. SEC traces of NB–PS$_{12k}$–NB and *mc*-PS$_{12k}$ obtained from cyclopolymerization (refractive index (RI) detection; eluent, THF; flow rate, 1.0 mL min^{-1}).

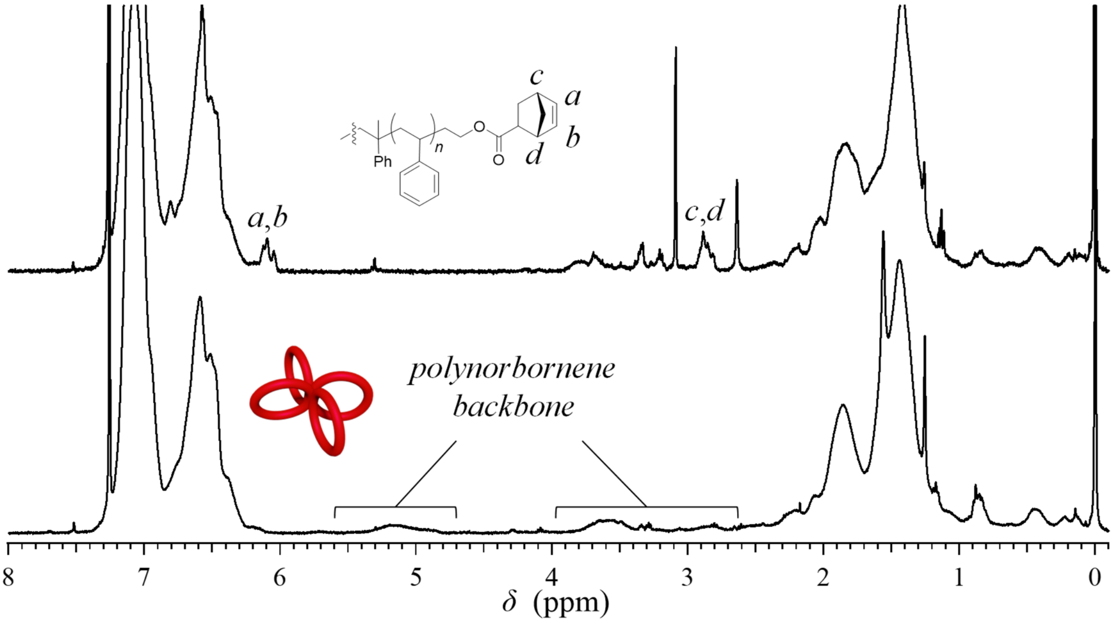


Figure S10. ^{1}H NMR spectra of NB–PS$_{6k}$–NB (upper) and *mc*-PS$_{6k}$ (run 8 in Table 2, lower) in CDCl$_3$.

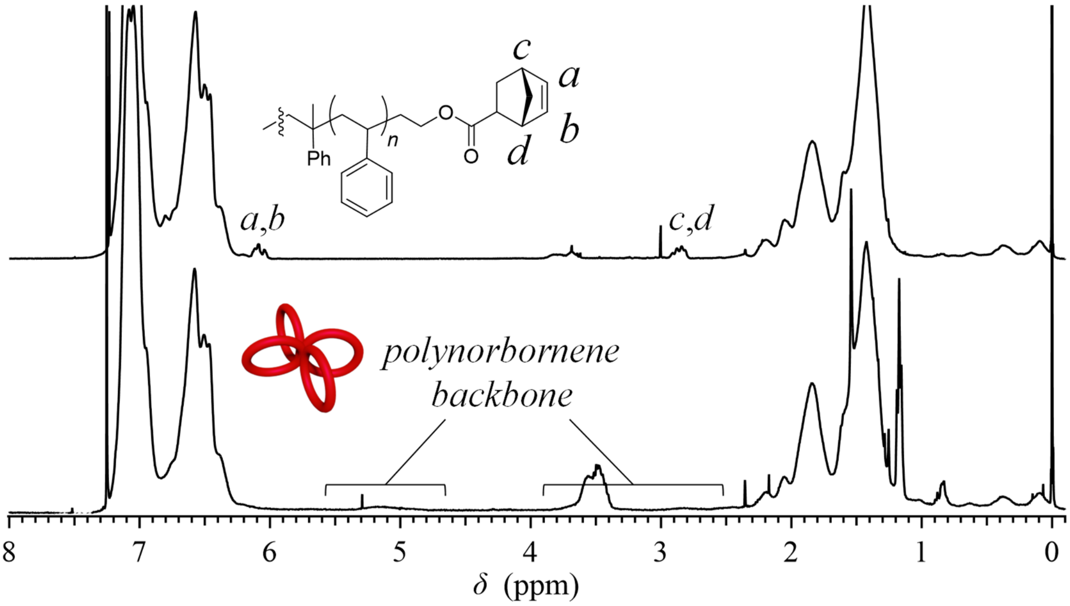


Figure S11. ^{1}H NMR spectra of NB–PS$_{12k}$–NB (upper) and *mc*-PS$_{12k}$ (run 11 in Table 2, lower) in CDCl$_3$.

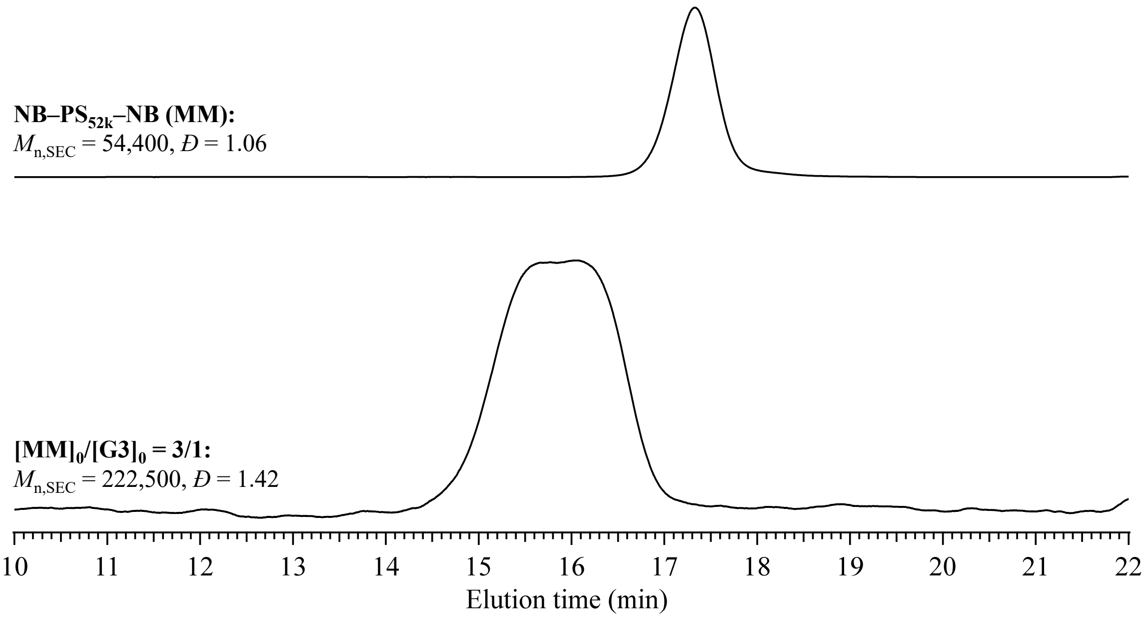


Figure S12. SEC traces of NB–PS$_{52k}$–NB and *mc*-PS$_{52k}$ obtained from SEC with higher exclusion limit (refractive index (RI) detection; eluent, THF; flow rate, 1.0 mL min^{-1}).

Gram-Scale Synthesis of *mc*-PS

Method B was used for the ROMP of NB–PS$_{13k}$–NB ($M_{n,MALS}$ = 13,400, 1.50 g, 112 μmol) with G3 (4.66 mL, 37.3 μmol as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in dry CH_2Cl_2 (746 mL) for 1.5 h to give *mc*-PS$_{13k}$ as a brown solid. Yield: 1.39 g (92.7%)

$M_{n,SEC}$ = 29,900, $Đ$ = 1.52, $M_{n,MALS}$ = 51,100, $Đ_{MALS}$ = 1.41, average number of cyclic units = 3.8

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.24–6.11 (m, *aromatic*), 5.81–4.78 (br, alkenyl of poly(norbornene) backbone), 3.94–3.36 (br, alkenyl of poly(norbornene) backbone), 2.99–2.72 (br, alkenyl of poly(norbornene) backbone), 2.44–1.67 (m, $–CH_2C\mathit{H}Ph–$), 1.67–0.99 (m, $–C\mathit{H}_2CHPh–$, $–CH_2CC\mathit{H}_3(Ph)–$, $–C\mathit{H}_2CCH_3(Ph)–$, $–C\mathit{H}_2CH_2OCO–$).

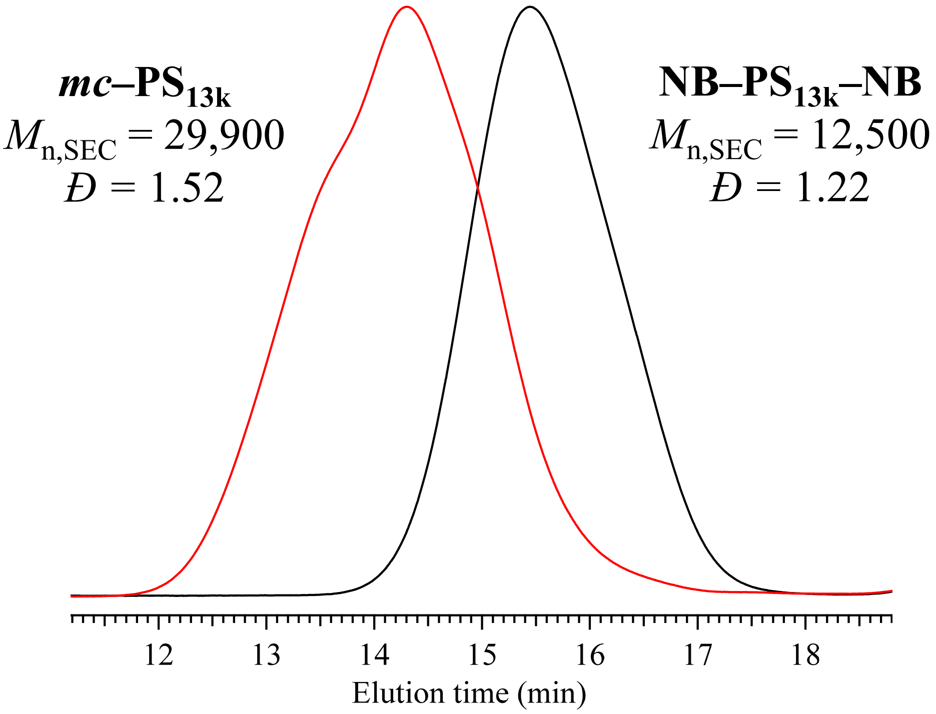


Figure S13. SEC traces of NB–PS$_{13k}$–NB (black) and *mc*-PS$_{13k}$ (red) (RI detection; eluent, THF).

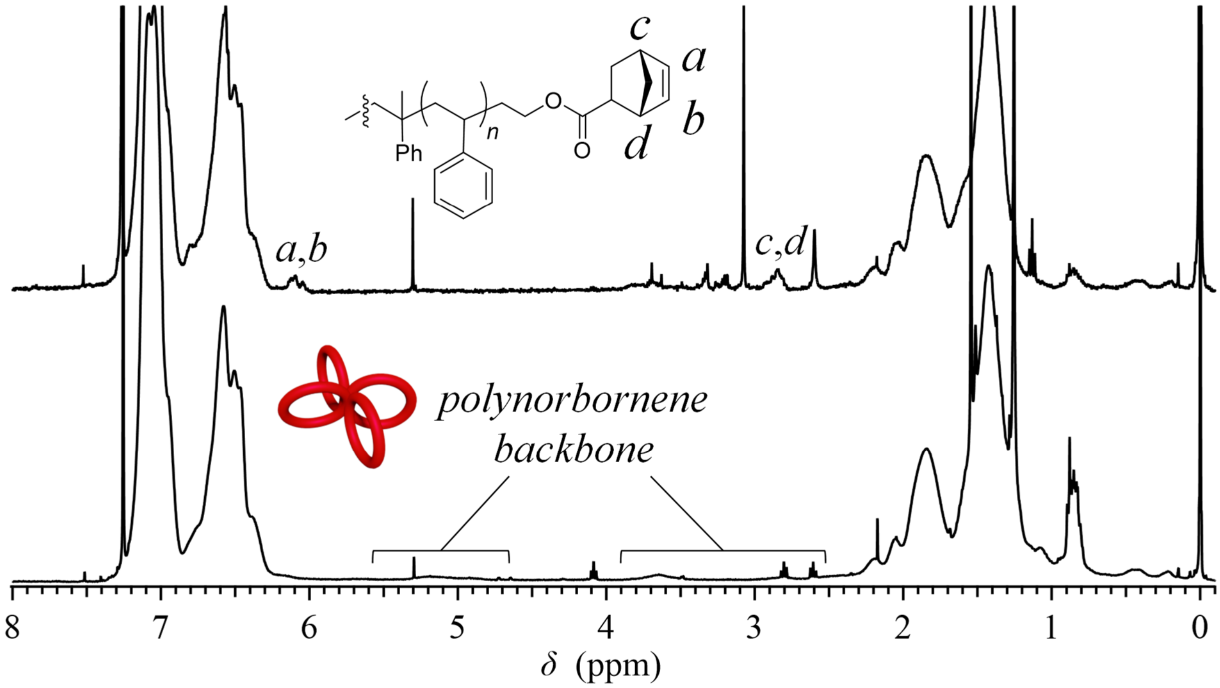


Figure S14. ^{1}H NMR spectra of NB–PS$_{13k}$–NB (upper) and *mc*-PS$_{13k}$ (lower) in CDCl$_3$.

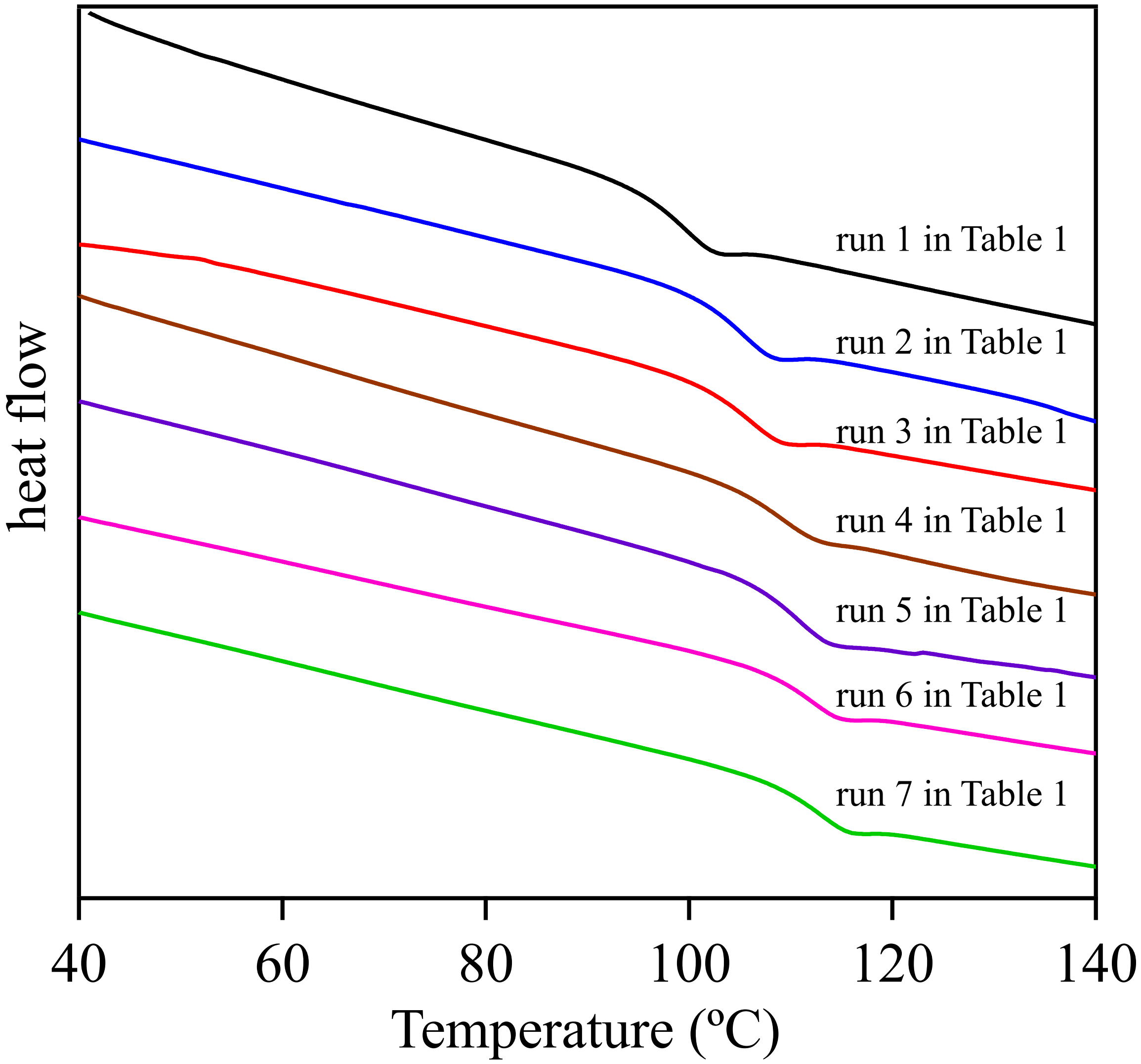


Figure S15. DSC curves of *mc*-PS$_{1k}$ during the second heating (heating rate: 10 °C min^{-1}).

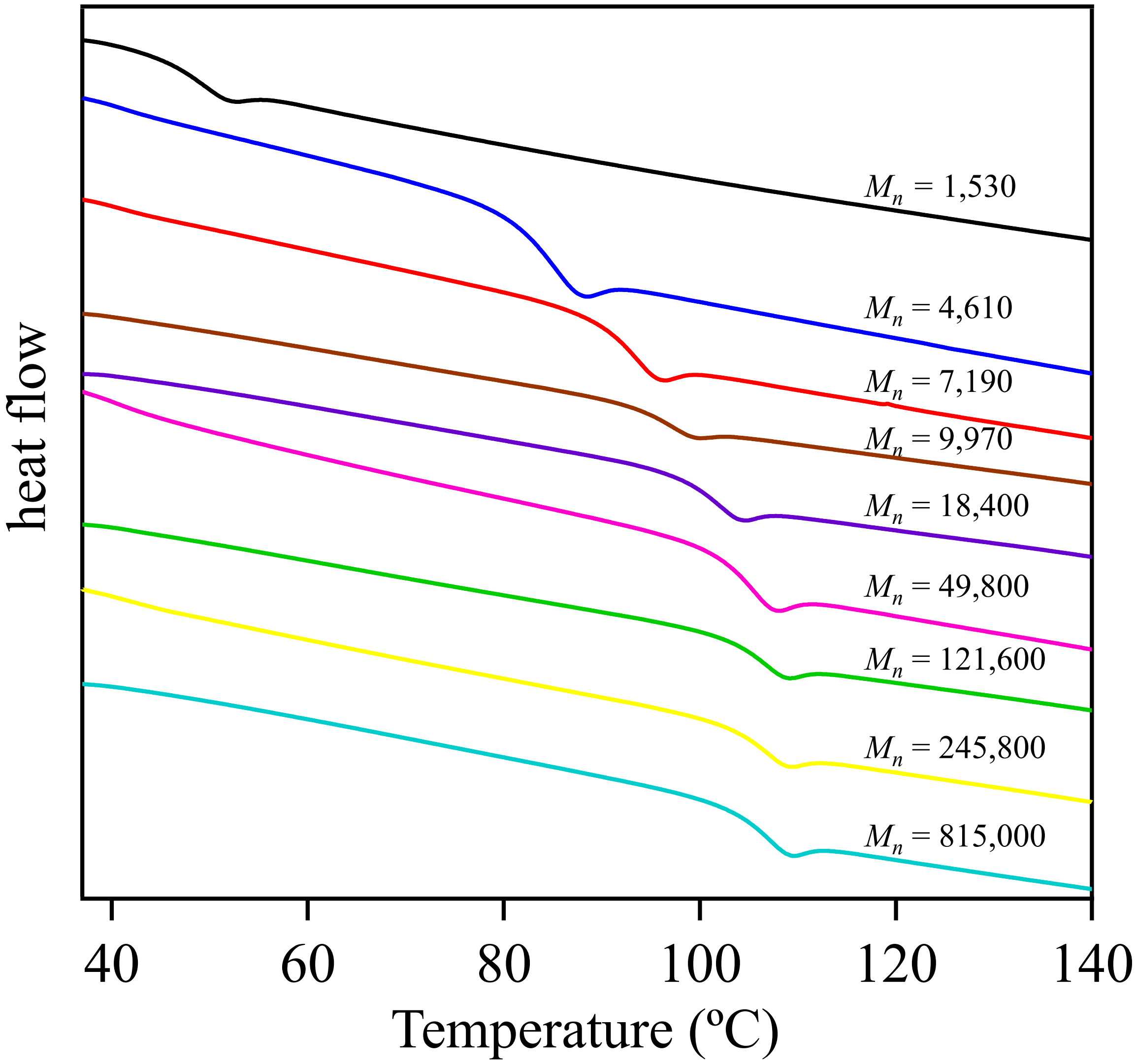


Figure S16. DSC curves of linear PS during the second heating (heating rate: 10 °C min^{-1}).

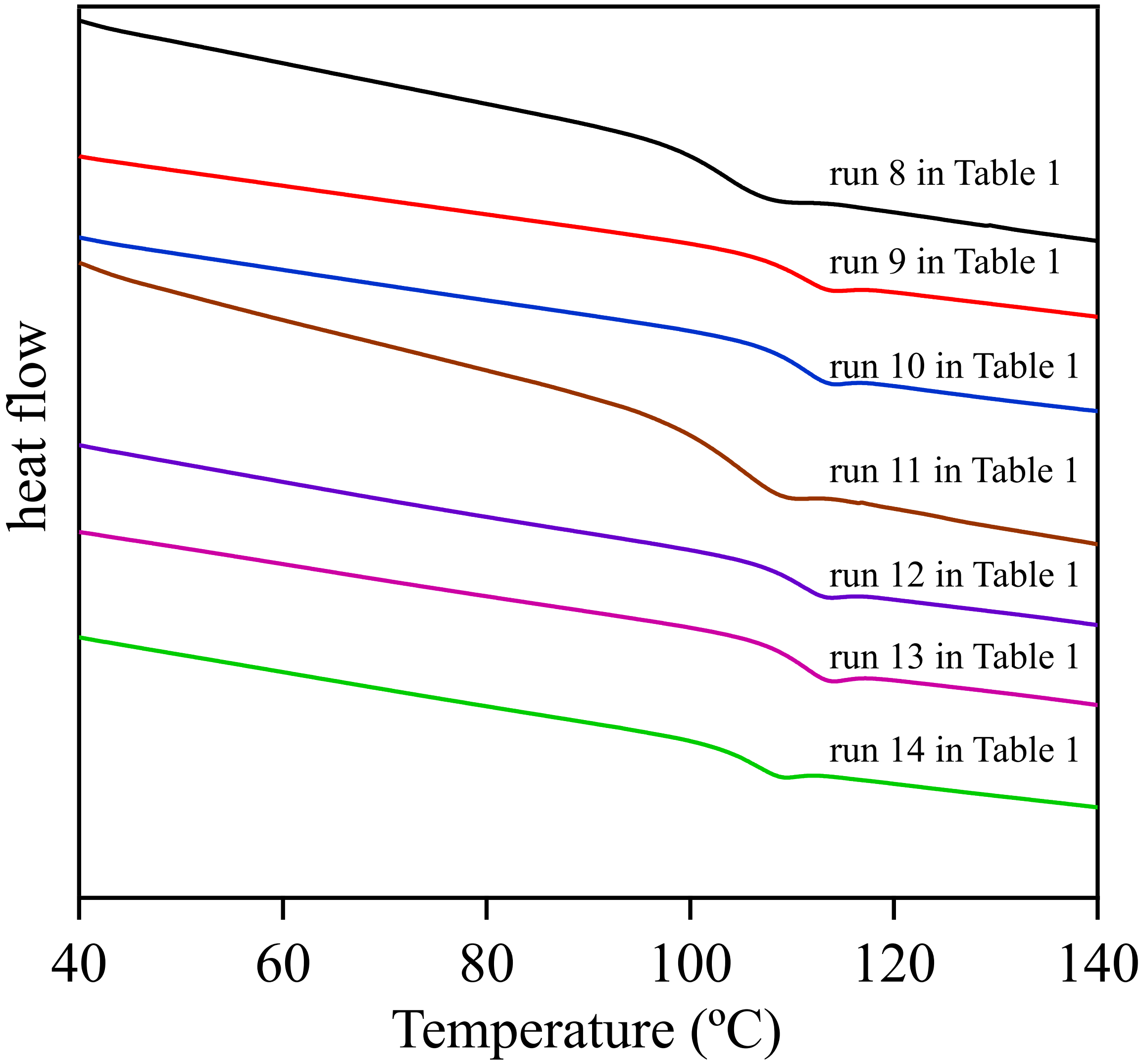
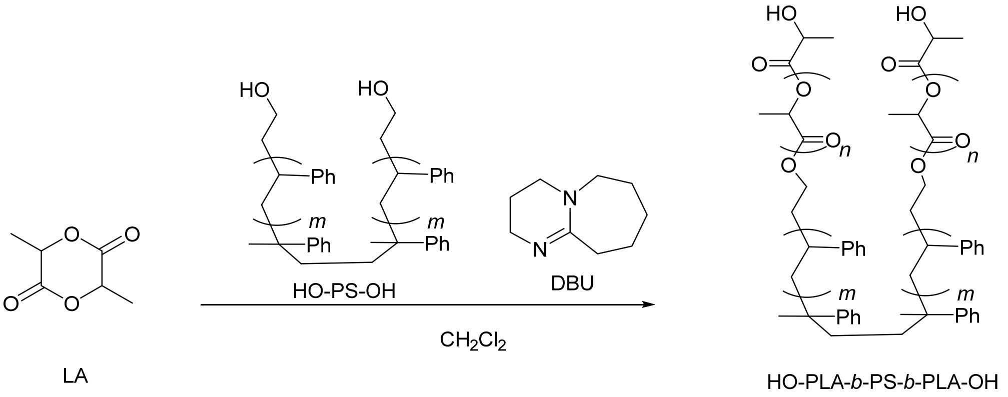


Figure S17. DSC curves of *mc*-PS$_{6k}$, *mc*-PS$_{12k}$, and *mc*-PS$_{52k}$ during the second heating (heating rate: 10 °C min^{-1}).

Synthesis of *α*, *ω*-end hydroxy-functionalized PLA-***block***-PS-***block***-PLA (HO–PLA-***b***-PS-***b***-PLA–OH)

Scheme S3. Synthesis of HO–PLA-*b*-PS-*b*-PLA–OH



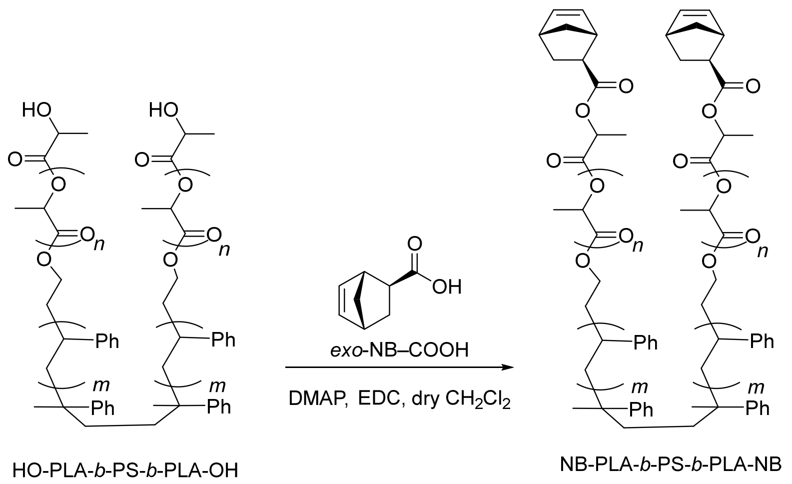
Typical procedure for the ring-opening polymerization of LA is as follows (method C): In a glovebox, HO–PS$_{6k}$–OH ($M_{n,NMR}$ = 6,000, 579 mg, 96.5 μmol) and LA (1.20 g, 8.32 mmol) were dissolved in CH_2Cl_2 (10.1 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU; 8.0 μL, 52 μmol) was then added to the CH_2Cl_2 solution to initiate the polymerization. After 50 sec, the polymerization was quenched by the addition of excess amount of benzoic acid. The mixture was purified by reprecipitation from CH_2Cl_2 to cold methanol to give HO–PLA-*b*-PS-*b*-PLA–OH as a white solid. Yield: 1.56 g (86.7%)

$M_{n,NMR}$ = 16,000, $M_{n,SEC}$ = 21,100, $Đ$ = 1.04

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.24–6.26 (m, *aromatic*), 5.28–5.08 (m, methine of PLA backbone), 3.88–3.63 (m, 4H, $–CH_2C\mathit{H}_2OCO–$), 2.77–2.60 (m, $–O\mathit{H}$), 2.23–1.72 (m, $–CH_2C\mathit{H}Ph–$), 1.72–1.16 (m, $–C\mathit{H}_2CHPh–$, $–CH_2CC\mathit{H}_3(Ph)–$, $–C\mathit{H}_2CCH_3(Ph)–$, $–C\mathit{H}_2CH_2OCO$, $CH_3C\mathit{H}_2)_2C(CH_2)O–$, $(C\mathit{H}_3CH_2)_2C(CH_2)O–$).

Synthesis of *α*, *ω*-end norbornenyl-functionalized PLA-*block*-PS-*block*-PLA (NB–PLA-*b*-PS-*b*-PLA–NB)

Scheme S4. Synthesis of NB–PLA-*b*-PS-*b*-PLA–NB



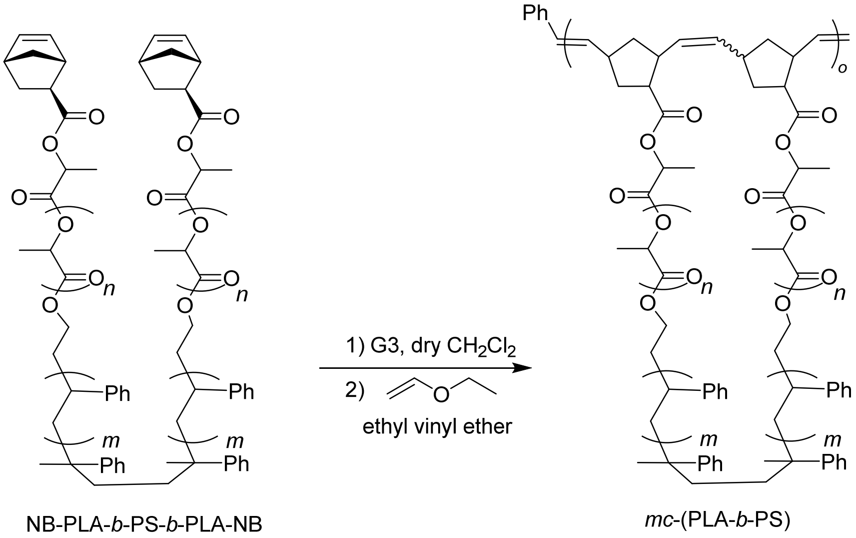
Method A was used for the reaction of HO–PLA-*b*-PS-*b*-PLA–OH ($M_{\mathrm{n,NMR}}$ = 16,000, 1.00 g, 62.5 μmol) with *exo*-NB-COOH (34.5 mg, 249 μmol), DMAP (45.8 mg, 375 μmol), and EDC (485 mg, 375 μmol) in CH_2Cl_2 (10.0 mL) for 81 h to give NB–PLA-*b*-PS-*b*-PLA–NB as a white solid. Yield: 831 mg (83.1%)

$M_{\mathrm{n,NMR}}$ = 15,900, $M_{\mathrm{n,SEC}}$ = 22,700, $Đ$ = 1.03, $M_{\mathrm{n,MALS}}$ = 12,700, $Đ_{\mathrm{MALS}}$ = 1.01

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.24–6.26 (m, *aromatic*), 6.16–6.07 (m, 4H, –C*H*=C*H*– in norbornene ring), 5.28–5.08 (m, methine of PLA backbone), 3.88–3.63 (m, 4H, –CH_2C*H*$_2$OCO–), 2.96–2.77 (m, 4H, –C*H*–CH_2–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 2.23–1.72 (m, –CH_2C*H*Ph–, *endo*-C*H*– of –CH–CH_2–CH–C*H*CO– in norbornene ring, *exo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring), 1.72–1.16 (m, –C*H*$_2$CHPh–, –CH_2CC*H*$_3$(Ph)–, –C*H*$_2$CCH_3(Ph)–, –C*H*$_2$$CH_2OCO, CH_3C*H*_2$)$_2$C(CH_2)O–, (C*H*$_3$$CH_2$)$_2$C($CH_2$)O–, –C*H*$_2$$CH_2$OCO–, *endo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring, bridge head –C*H*$_2$– in norbornene ring).

Synthesis of *mc*-(PLA-*b*-PS)

Scheme S5. Synthesis of *mc*-(PLA-*b*-PS)



Method B was used for the ROMP of NB–PLA-*b*-PS-*b*-PLA–NB ($M_{n,NMR}$ = 15,900, 50.0 mg, 3.14 μmol) with G3 (131 μL, 1.04 μmol as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in dry CH_2Cl_2 (21.0 mL) for 1.5 h to give *mc*-(PLA-*b*-PS) as a brown solid. Yield: 49.8 mg (99.6%)

$M_{n,SEC}$ = 55,200, $Đ$ = 1.82, $M_{n,MALS}$ = 66,400, $Đ_{MALS}$ = 1.44, average number of cyclic units = 5.2

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.24–6.26 (m, *aromatic*), 5.28–5.08 (m, methine of PLA backbone), 4.05–2.52 (br, alkenyl of poly(norbornene), 3.88–3.63 (m, 4H, $–CH_2CH_2OCO–$), 2.23–1.72 (m, $–CH_2CHPh–$), 1.72–1.16 (m, $–CH_2CHPh–$, $–CH_2CCH_3(Ph)–$, $–CH_2CCH_3(Ph)–$, $–CH_2CH_2OCO$, $CH_3CH_2)_2C(CH_2)O–$, $(CH_3CH_2)_2C(CH_2)O–$).

Table S1. Molecular characterization of *mc*-(PLA-*b*-PS) [a]

run	$[\mathrm{MM}]_0/[\mathrm{G3}]_0$	$[\mathrm{MM}]_0$ (mM)	time (min)	$M_{\mathrm{n,MALS}}$ [b]	$Đ$ [c]	number of cyclc unit [d]	yield (%)
15	3/1	0.150	90	66,400	1.82	5.2	99.6
16	6/1	0.150	300	80,400	1.61	6.3	97.2
17	9/1	0.150	300	112,100	1.59	8.8	94.4

[a] Polymerization conditions: temperature, r.t.; atmosphere, Ar; solvent, CH_2Cl_2. [b] Determined by SEC-MALS-Visco in chloroform. [c] Determined by SEC in tetrahydrofuran (THF) using PS as the standard. [d] The average number of cyclic units in the obtained *mc*-(PLA-*b*-PS) was estimated as (M_n of *mc*-(PLA-*b*-PS))/(M_n of NB–PLA-*b*-PS-*b*-PLA–NB).

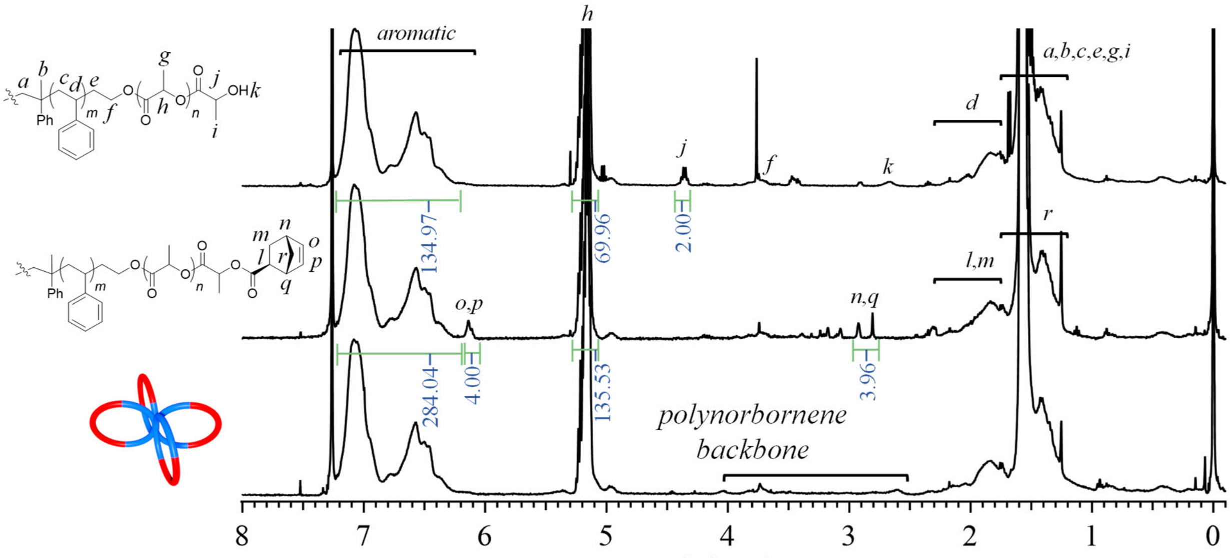


Figure S18. ^{1}H NMR spectra of HO–PLA-*b*-PS-*b*-PLA–OH (upper), NB–PLA-*b*-PS-*b*-PLA–NB (middle), and *mc*-(PLA-*b*-PS) (lower) in $CDCl_3$.

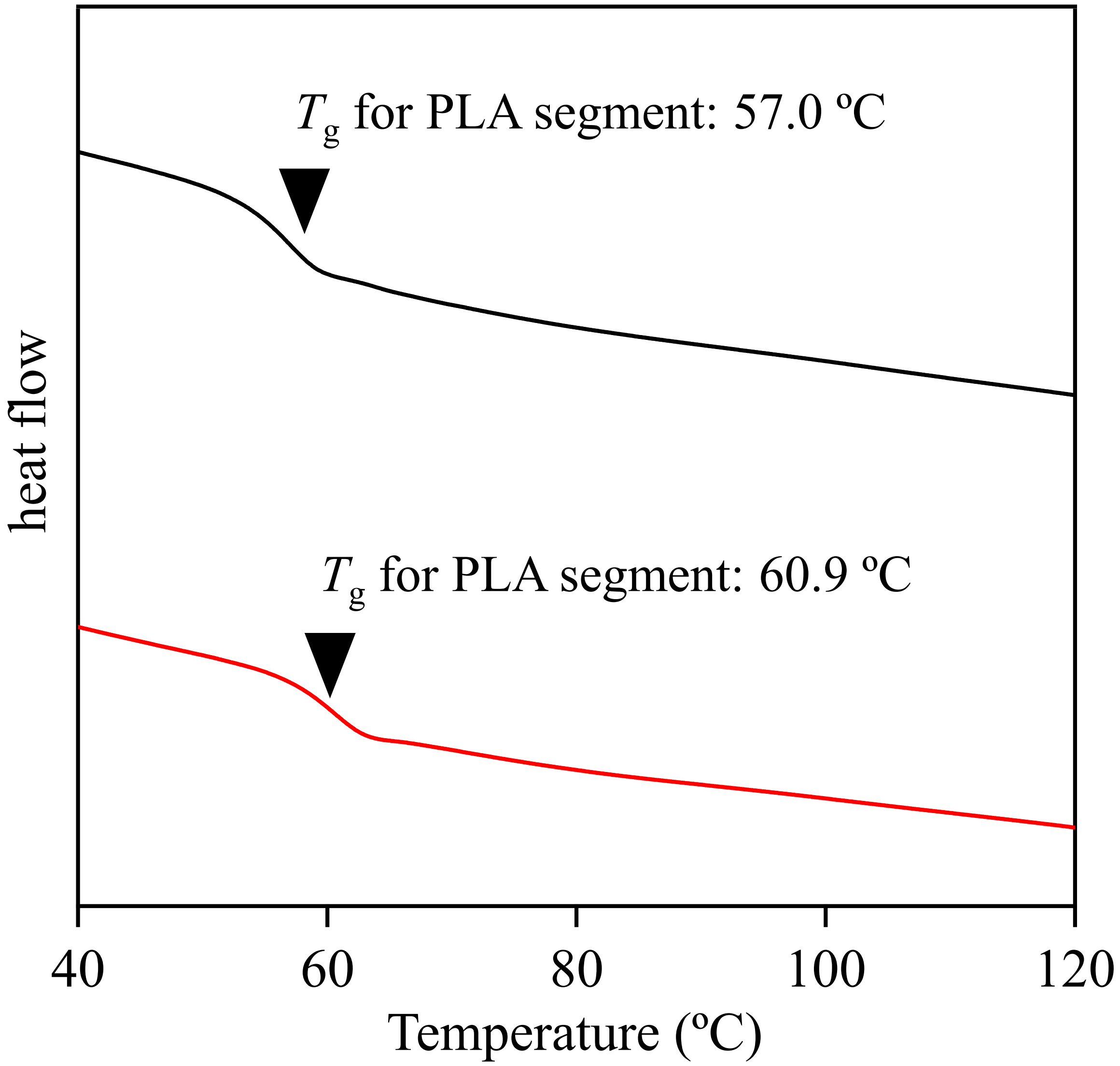
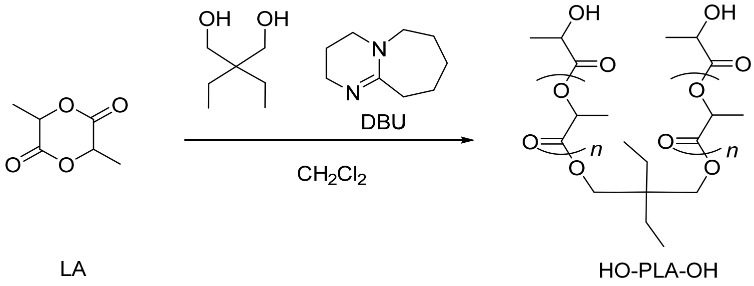


Figure S19. DSC curves during second heating process of NB–PLA-*b*-PS-*b*-PLA–NB (black) and *mc*-(PS-*b*-PLA) (run 15 in **Table S1**, red).

Synthesis of *α*, *ω*-end hydroxy-functionalized PLA (HO–PLA$_{6k}$–OH)

Scheme S6. Synthesis of HO–PLA–OH



Typical procedure for the ring-opeming polymerization of LA is as follows (method C): In a glovebox, 2,2-diethyl-1,3-propanediol (29.8 mg, 226 μmol) and LA (1.50 g, 10.4 mmol) were dissolved in CH_2Cl_2 (10.4 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU; 15.9 μL, 104 μmol) was then added to the CH_2Cl_2 solution to initiate the polymerization. After 4 min, the polymerization was quenched by the addition of excess amount of benzoic acid. The mixture was purified by a preparative GPC give HO–PLA$_{6k}$–OH as a white solid. Yield: 1.46 g (97.3%)

$M_{n,NMR}$ = 6,400, $M_{n,SEC}$ = 12,000, $Đ$ = 1.07

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 5.29–5.04 (m, methine of PLA backbone), 4.42–4.28 (m, methine of *α*, *ω*-chain end lactyl unit), 4.04–3.86 (m, $(CH_3CH_2)_2C(CH_2)O$–) 2.73–2.63 (m, –O*H*), 1.79–1.44 (methyl of PLA backbone), 1.35–1.17 (m, $(CH_3CH_2)_2C(CH_2)O$–), and 0.92–0.75 (m, $(CH_3CH_2)_2C(CH_2)O$–).

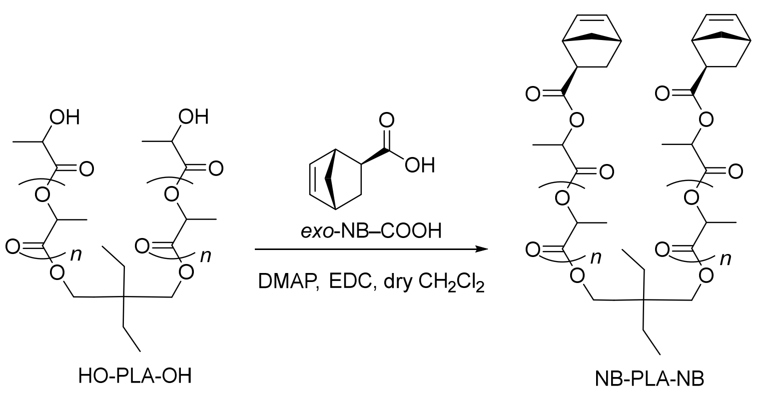
Method C was used for the polymerization of LA (1.50 g, 10.4 mmol) with 2,2-diethyl-1,3-propanediol (11.0 mg, 83.1 μmol) and DBU (15.9 μL, 104 μmol) in CH_2Cl_2 (10.4 mL) for 4 min to give HO–PLA_{13k}–OH as a white solid.Yield: 1.25 g (83.3%)

$M_{n,NMR}$ = 12,700, $M_{n,SEC}$ = 19,300, $Đ$ = 1.04

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 5.27–5.04 (m, methine of PLA backbone), 4.41–4.29 (m, methine of α, ω-chain end lactyl unit), 4.01–3.88 (m, $(CH_3CH_2)_2C(CH_2)O$–) 2.74–2.62 (m, –OH), 1.79–1.44 (methyl of PLA backbone), 1.35–1.17 (m, $(CH_3C\mathit{H}_2)_2C(CH_2)O$–), and 0.97–0.75 (m, $(C\mathit{H}_3CH_2)_2C(CH_2)O$–).

Synthesis of *α*, *ω*-end norbornenyl-functionalized PLA (NB–PLA$_{6k}$–NB)

Scheme S7. Synthesis of NB–PLA–NB



Method A was used for the reaction of HO–PLA$_{6k}$–OH ($M_{n,NMR}$ = 6,700, 1.00 g, 149 μmol) with *exo*-NB–COOH (44.3 mg, 321 μmol), DMAP (58.6 mg, 493 μmol), and EDC (94.6 mg, 480 μmol) in CH$_2$Cl$_2$ (10.0 mL) for 2 days to give NB–PLA$_{6k}$–NB as a white solid. Yield: 930 mg (93.0%)

$M_{n,NMR}$ = 6,700, $M_{n,SEC}$ = 12,100, $Đ$ = 1.08

^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 6.15–6.00 (m, 4H, –C*H*=C*H*– in norbornene ring), 5.02-4.49 (m, methine of PLLA backbone), 3.90–3.54 (m, 4H, –CH$_2$C*H*$_2$OCO–), 2.94–2.83 (m, 4H, –C*H*–CH$_2$–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 2.48–1.66 (*endo*-C*H*– of –CH–CH$_2$–CH–C*H*CO– in norbornene ring, *exo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring), 1.66–1.15 (m, –C*H*$_2$CH$_2$OCO–, *endo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring, bridge head –C*H*$_2$– in norbornene ring, methyl of PLA backbone), and 0.92–0.75 (m, (C*H*$_3$CH$_2$)$_2$C(CH$_2$)O–).

Method A was used for the reaction of HO–PLA$_{13k}$–OH ($M_{n,NMR}$ = 12,700, 1.00 g, 78.7 μmol) with *exo*-NB–COOH (48.5 mg, 351 μmol), DMAP (59.0 mg, 483 μmol), and EDC (95.1 mg, 496 μmol) in CH_2Cl_2 (10.0 mL) for 2 days to give NB–PLA$_{13k}$–NB as a white solid. Yield: 911 mg (91.1%)

$M_{n,NMR}$ = 13,200, $M_{n,SEC}$ = 19,800, $Đ$ = 1.03

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.15–6.00 (m, 4H, –C*H*=C*H*– in norbornene ring), 5.02-4.49 (m, methine of PLLA backbone), 3.90–3.54 (m, 4H, –CH_2CH_2OCO–), 2.94–2.83 (m, 4H, –C*H*–CH_2–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 2.48–1.66 (*endo*-C*H*– of –CH–CH_2–CH–C*H*CO– in norbornene ring, *exo*-C*H*– of –CH–CH_2–CH–CO– in norbornene ring), 1.66–1.15 (m, –CH_2CH_2OCO–, *endo*-C*H*– of –CH–CH_2–CH–CO– in norbornene ring, bridge head –CH_2– in norbornene ring, methyl of PLA backbone), and 0.92–0.75 (m, $(CH_3CH_2)_2C(CH_2)O$–).

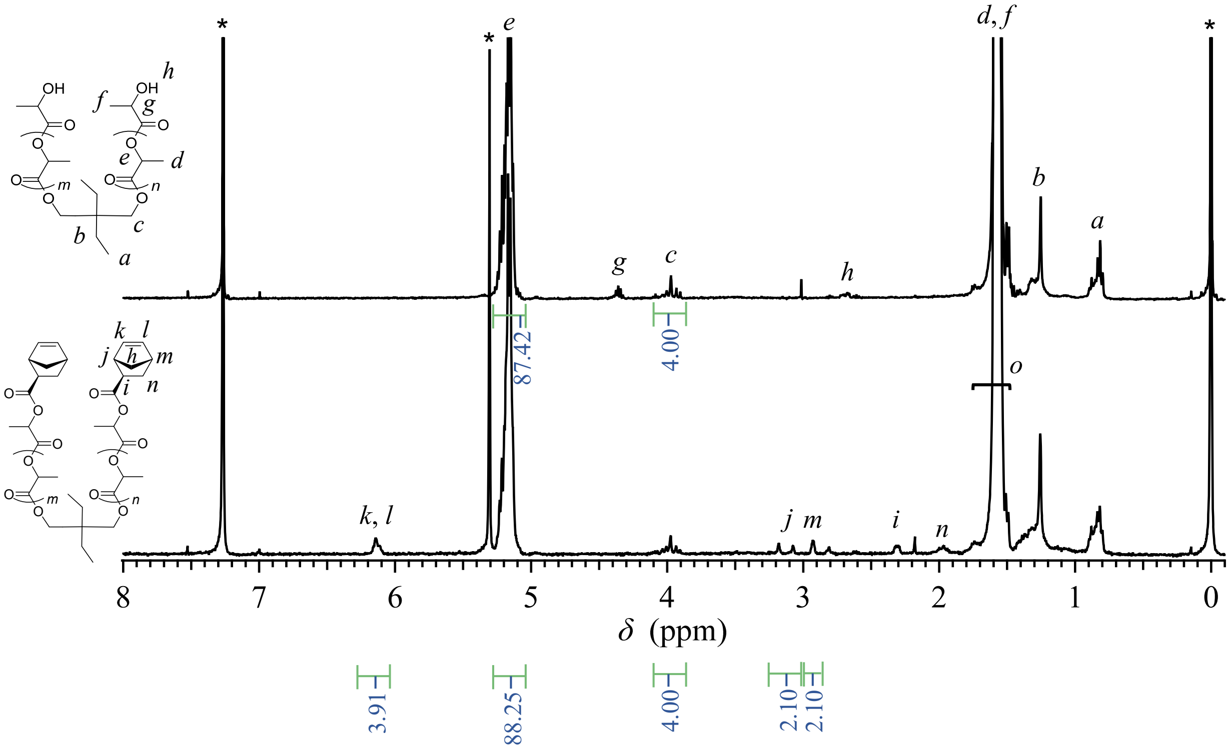


Figure S20. ^{1}H NMR spectra of HO–PLA$_{6k}$–OH (upper) and NB–PLA$_{6k}$–NB (lower) in CDCl$_3$.

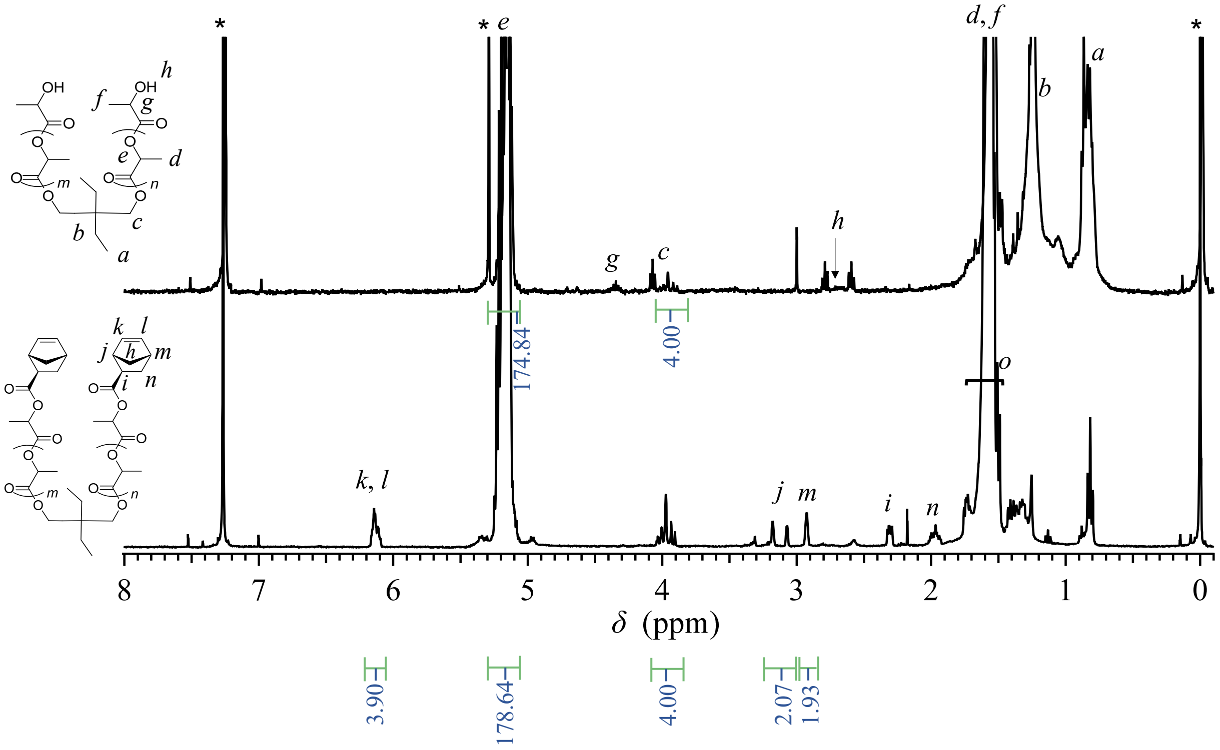
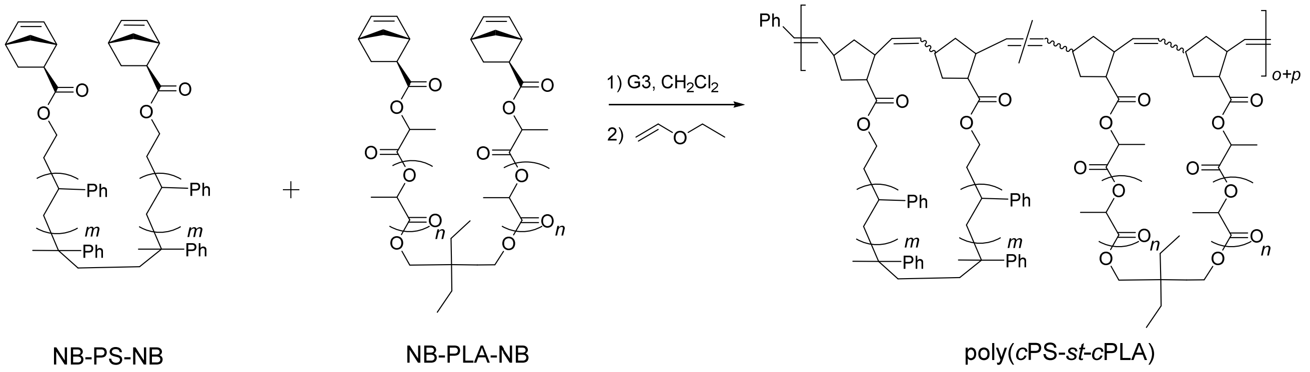


Figure S21. ^{1}H NMR spectra of HO–PLA$_{13k}$–OH (upper) and NB–PLA$_{13k}$–NB (lower) in CDCl$_3$.

Statistical cyclocopolymerization of NB–PS–NB and NB–PLA–NB

Scheme S8. Synthesis of poly(*c*PS-*st*-*c*PLA)



Method B was used for the ROMP of NB-PS$_{6k}$-NB ($M_{\text{n.NMR}}$ = 5,700, 50.0 mg, 8.77 μmol) and NB-PLA$_{6k}$-NB ($M_{\text{n,NMR}}$ = 6,700, 50.0 mg, 7.46 μmol) with G3 (1.01 mL, 8.06 μmol as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in dry CH_2Cl_2 (129 mL) for 3h to give poly(*c*PS-*st*-*c*PLA) as a brown solid.Yield: 81.7 mg (81.7%)

$M_{\text{n,SEC}}$ = 15,300, $Đ$ = 1.34, $M_{\text{n,MALS}}$ = 23,800, $Đ_{\text{MALS}}$ = 1.07, average number of cyclic units = 3.8

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38–6.25 (m, *aromatic*), 5.02-4.49 (m, methine of PLLA backbone), 4.31–2.48 (br, alkenyl of poly(norbornene), 2.44–0.75 (m, –$CH_2C\mathit{H}Ph$–, –$C\mathit{H}_2CHPh$–, –$CH_2CC\mathit{H}_3(Ph)$–, –$C\mathit{H}_2CCH_3(Ph)$–, –$C\mathit{H}_2CH_2OCO$–, –$C\mathit{H}_2CH_2OCO$–, methyl of PLA backbone, $(C\mathit{H}_3CH_2)_2C(CH_2)O$–).

Table S2. Molecular characterization of poly(*c*PS-*st*-*c*PLA) [a]

run	MM	$[PS]_0/[PLA]_0/[G3]_0$	$[PS+PLA]_0$ (mM)	time (min)	$M_{n,MALS}$ [b]	$Đ$ [c]	number of cyclc unit [d]	yield (%)
18	NB–PS$_{6k}$–NB ($M_{n,MALS}$ = 6,470) and NB–PLA$_{6k}$–NB ($M_{n,MALS}$ = 6,700)	1/1/1	0.125	120	23,800	1.34	3.8	81.7
19		2/2/1	0.125	210	27,000	1.19	4.4	50.4
20		3/3/1	0.150	120	40,300	1.29	6.5	92.2
21	NB–PS$_{13k}$–NB ($M_{n,MALS}$ = 13,400) and NB–PLA$_{13k}$–NB ($M_{n,MALS}$ = 13,200)	1/1/1	0.125	180	45,000	1.54	3.5	61.1
22		2/2/1	0.150	120	62,700	1.47	4.9	88.2
23		3/3/1	0.200	300	117,600	1.47	9.2	52.8

[a] Polymerization conditions: temperature, r.t.; atmosphere, Ar; solvent, CH_2Cl_2. [b] Determined by SEC-MALS-Visco in chloroform. [c] Determined by SEC in tetrahydrofuran (THF) using PS as the standard. [d] The average number of cyclic units in the obtained poly(*c*PS-*st*-*c*PLA) was estimated as (M_n of poly(*c*PS-*st*-*c*PLA))/(M_n of NB–PS–NB + NB–PLA–NB).

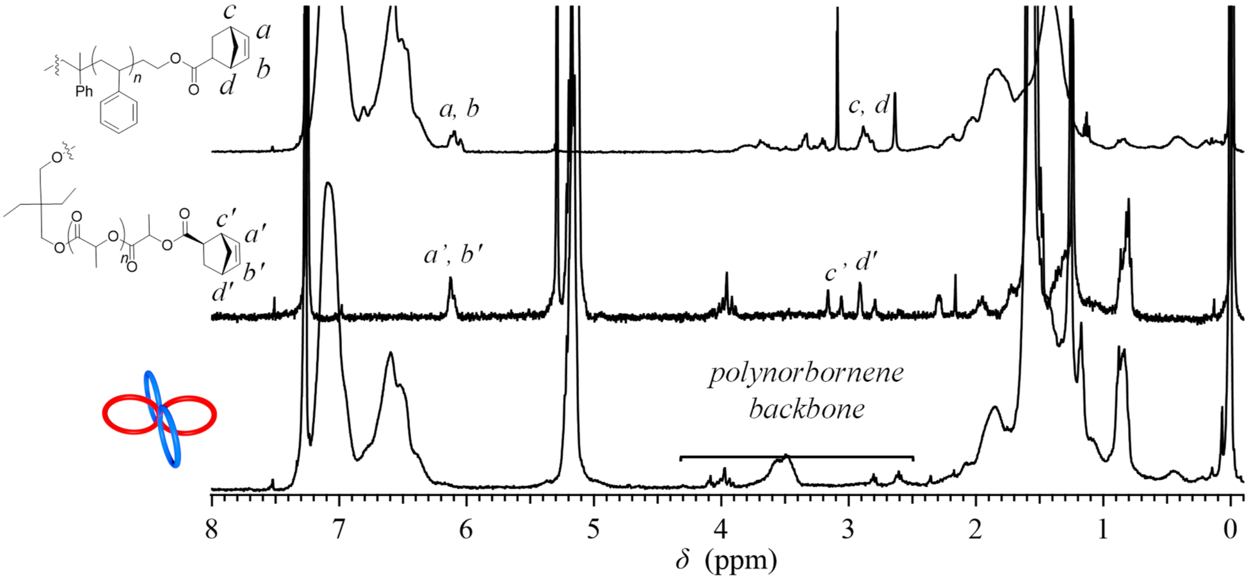
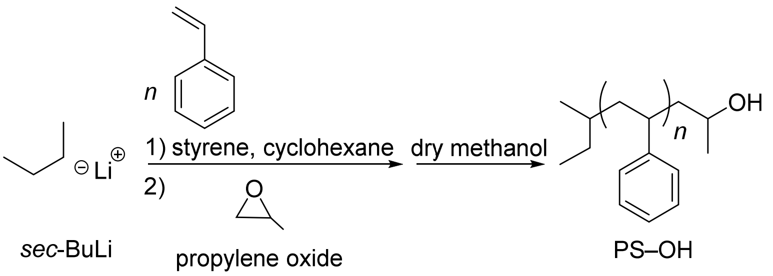


Figure S22. ^{1}H NMR spectra of NB–PS$_{6k}$–NB (upper), NB–PLA$_{6k}$–NB (middle), and poly(*c*PS-*st*-*c*PLA) (lower) in $CDCl_3$.

Synthesis of *ω*-end hydroxy-functionalized PS (PS_{3k}–OH)

Scheme S9. Synthesis of PS–OH



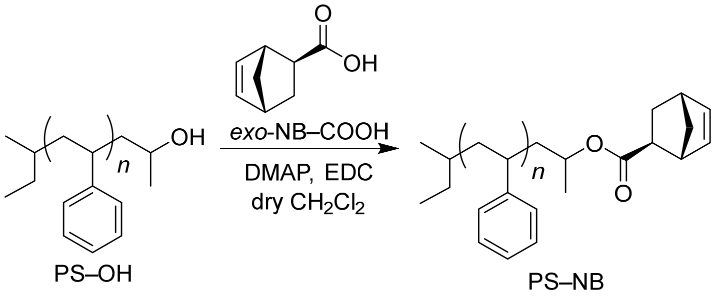
Under Ar atmosphere, cyclohexane (24.0 mL) was placed in a round-bottom flask equipped with a greaseless valve and then heated to 40 °C in an oil bath. *sec*-BuLi (953 µL, 857 µmol) was added to the solution. Styrene (2.76 mL, 24.0 mmol) was added to the solution, and the mixture was stirred for 2 h. Propylene oxide (600 µL, 8.57 mmol) was then added to the solution at 40 °C, and the mixture was stirred for 2 h. Excess dry methanol was added to terminate the polymerization. The product was purified by reprecipitation in methanol to give PS_{3k}–OH as a white solid. Yield: 2.49 g (99.6%)

$M_{n,NMR}$ = 2,900, $M_{n,SEC}$ = 3,200, $Đ$ = 1.10

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.22–6.22 (m, *aromatic*), 3.61–3.16 (s, 1H, $–CH_2C\mathit{H}(CH_3)OH$), 2.44–1.66 (m, $–CH_2C\mathit{H}Ph–$), 1.66–1.21 (m, $–C\mathit{H}_2CHPh–$, $–C\mathit{H}_2CH(CH_3)OH$, $–CH_2CH(C\mathit{H}_3)OH$), 1.14–0.51 (m, –*sec*-butyl).

Synthesis of PS_{3k}–NB

Scheme S10. Synthesis of PS–NB



Method A was used for the reaction of PS–OH ($M_{n,NMR}$ = 2,900, 2.30 g, 793 μmol) with *exo*-NB–COOH (268 mg, 1.94 mmol), DMAP (351 mg, 2.87 mmol), and EDC (559 mg, 2.92 mmol) in CH_2Cl_2 (24 mL) for 4 days to give PS_{3k}–NB as a white solid. Yield: 1.73 g (75.2%)

$M_{n,NMR}$ = 3,300, $M_{n,SEC}$ = 3,300, $Đ$ = 1.04, $M_{n,MALS}$ = 5,100, $Đ_{MALS}$ = 1.01

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.22–6.19 (m, *aromatic*), 6.19–5.96 (m, 2H, –C*H*=C*H*– in norbornene ring), 4.78–4.34 (s, 1H, –CH_2C*H*(CH_3)O–), 2.97–2.72 (m, 2H, –C*H*–CH_2–CH–CO– in norbornene ring, –C*H*–CH–CO– in norbornene ring), 2.44–1.68 (m, –CH_2C*H*Ph–, *endo*-C*H*– of –CH–CH_2–CH–C*H*CO– in norbornene ring, *exo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring, bridge head –C*H*$_2$– in norbornene ring), 1.68–1.09 (m, –C*H*$_2$CHPh–, –C*H*$_2$CH(CH_3), –CH_2CH(C*H*$_3$), *endo*-C*H*– of –CH–C*H*$_2$–CH–CO– in norbornene ring), 1.08–0.51 (m, –*sec*-butyl).

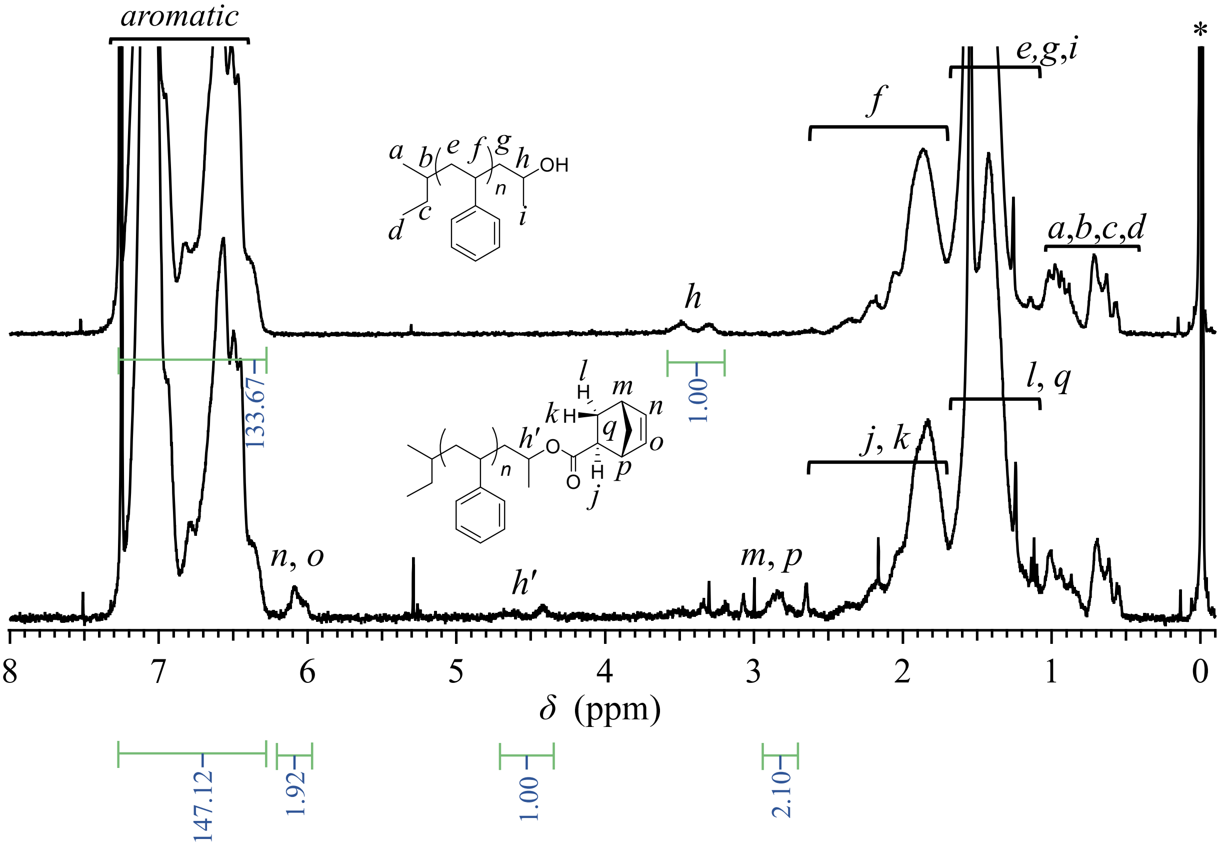
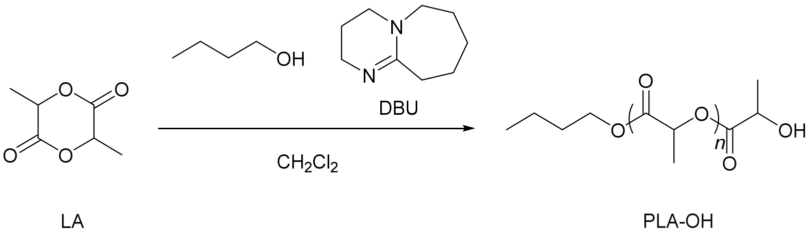


Figure S23. ^{1}H NMR spectra of PS$_{3k}$–OH (upper) and PS$_{3k}$–NB (lower) in CDCl$_3$.

Synthesis of *ω*-end norbornenyl-functionalized PLA (PLA_{3k}–OH)

Scheme S11. Synthesis of PLA–OH



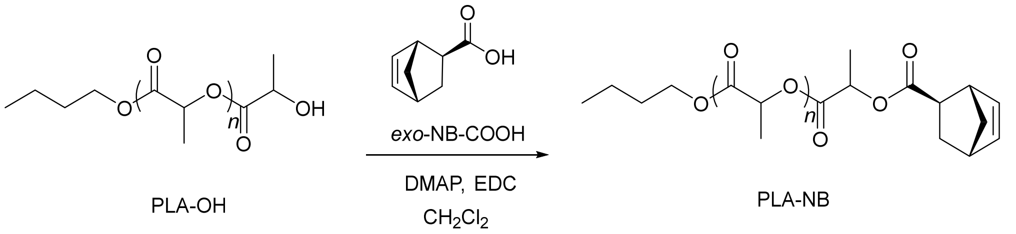
Method A was used for the polymerization of LA (1.50 g, 10.4 mmol) with 1-butanol (29.6 mg, 399 μmol) and DBU (15.9 μL, 104 μmol) in CH_2Cl_2 (10.4 mL) for 1 min to give PLA_{3k}-OH as a white solid. Yield: 859 mg (69.3%)

$M_{n,NMR}$ = 2,700, $M_{n,SEC}$ = 4,700, $Đ$ = 1.10

^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 5.27–5.04 (m, methine of PLA backbone), 4.41–4.29 (m, methine of *ω*-chain end lactyl unit), 2.74–2.62 (m, –OH), 1.79–1.44 (methyl of PLA backbone), 1.35–1.17 (m, $CH_3CH_2CH_2CH_2O$–), 1.35–1.17 (m, $CH_3CH_2CH_2CH_2O$–), 1.35–1.17 (m, $CH_3CH_2CH_2CH_2O$–), and 0.97–0.75 (m, $CH_3CH_2CH_2CH_2O$–).

Synthesis of ω-end norbornenyl-functionalized PLA (PLA$_{3k}$–NB)

Scheme S12. Synthesis of PLA–NB



Method A was used for the reaction of PLA$_{3k}$-OH ($M_{\mathrm{n,NMR}}$ = 2,700, 500 mg, 185 μmol) with *exo*-NB-COOH (53.4 mg, 387 μmol), DMAP (68.7 mg, 562 μmol), and EDC (112 mg, 583 μmol) in CH_2Cl_2 (5.0 mL) for 2 days to give PLA$_{3k}$-NB as a white solid. Yield: 491 mg (98.2%)

$M_{\mathrm{n,NMR}}$ = 3,000, $M_{\mathrm{n,SEC}}$ = 5,300, $Đ$ = 1.08

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.19–6.08 (m, 2H, $-\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}-$ in norbornene ring), 5.27–5.04 (m, methine of PLA backbone), 4.41–4.29 (m, methine of ω-chain end lactyl unit), 3.19–2.89 (m, 2H, $-\mathrm{C}\mathit{H}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CO}-$ in norbornene ring, $-\mathrm{C}\mathit{H}-\mathrm{CH}-\mathrm{CO}-$ in norbornene ring), 2.38–1.90 (*endo*-$\mathrm{C}\mathit{H}-$ of $-\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{C}\mathit{H}\mathrm{CO}-$ in norbornene ring, *exo*-$\mathrm{C}\mathit{H}-$ of $-\mathrm{CH}-\mathrm{C}\mathit{H}_2-\mathrm{CH}-\mathrm{CO}-$ in norbornene ring), 1.79–1.44 ($-\mathrm{C}\mathit{H}_2\mathrm{CH_2OCO}-$, *endo*-$\mathrm{C}\mathit{H}-$ of $-\mathrm{CH}-\mathrm{C}\mathit{H}_2-\mathrm{CH}-\mathrm{CO}-$ in norbornene ring, bridge head $-\mathrm{C}\mathit{H}_2-$ in norbornene ring, methyl of PLA backbone), 1.35–1.17 (m, $\mathrm{CH_3CH_2C}\mathit{H}_2\mathrm{CH_2O}-$), 1.35–1.17 (m, $\mathrm{CH_3C}\mathit{H}_2\mathrm{CH_2CH_2O}-$), 1.35–1.17 (m, $\mathrm{CH_3CH_2C}\mathit{H}_2\mathrm{CH_2O}-$), and 0.97–0.75 (m, $\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2CH_2O}-$).

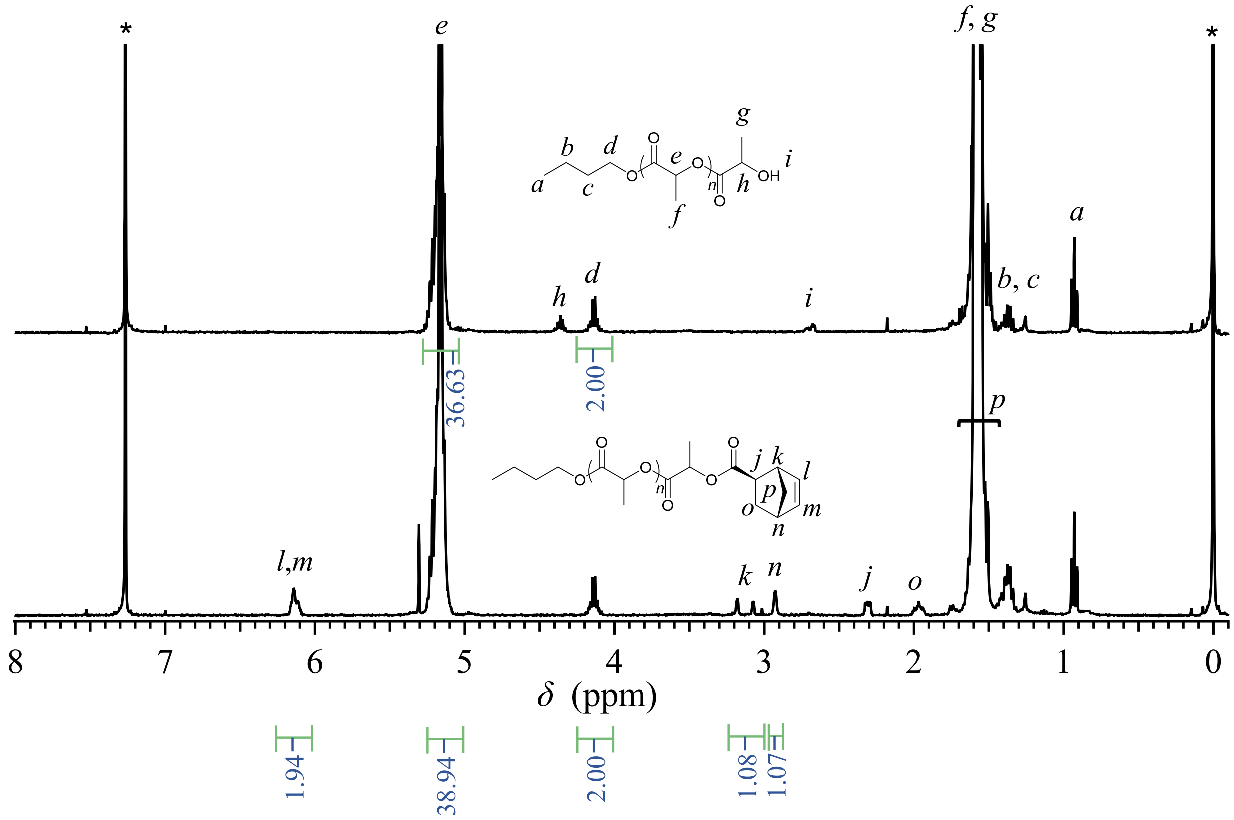
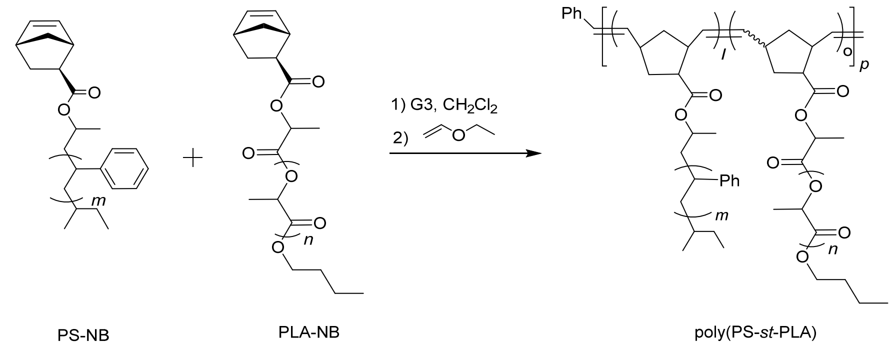


Figure S24. ^{1}H NMR spectra of PLA$_{3k}$–OH (upper) and PLA$_{3k}$–NB (lower) in CDCl$_3$.

Statistical cyclocopolymerization of PS–NB and PLA–NB

Scheme S13. Synthesis of poly(PS-*st*-PLA)



Method B was used for the ROMP of PS_{3k}-NB (50.0 mg, 13.9 μmol) and PLA_{3k}-NB (50.0 mg, 16.7 μmol) with G3 (316 μL, 2.53 μmol as a 8.0 mmol L^{-1} solution in CH_2Cl_2) in dry CH_2Cl_2 (1.52 mL) for 2.0 h to give poly(PS-*st*-PLA) as a brown solid. Yield: 76.7 mg (76.7%)

$M_{n,SEC}$ = 28,200, $Đ$ = 1.07, $M_{n,MALS}$ = 33,800, $Đ_{MALS}$ = 1.02, average number of cyclic units = 10.7

^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.22–6.19 (m, *aromatic*), 5.27–5.04 (m, methine of PLA backbone), 4.78–4.34 (s, 1H, $–CH_2C\mathit{H}(CH_3)O–$), 4.41–4.29 (m, methine of ω-chain end lactyl unit), 4.32–2.52 (br, alkenyl of poly(norbornene), 2.44–0.51 (m, $–CH_2C\mathit{H}Ph–$, methyl of PLA backbone, $–C\mathit{H}_2CHPh–$, $–C\mathit{H}_2CH(CH_3)$, $–CH_2CH(C\mathit{H}_3)$, $CH_3C\mathit{H}_2CH_2CH_2O–$, $CH_3CH_2C\mathit{H}_2CH_2O–$, –*sec*-butyl, $C\mathit{H}_3CH_2CH_2CH_2O–$).

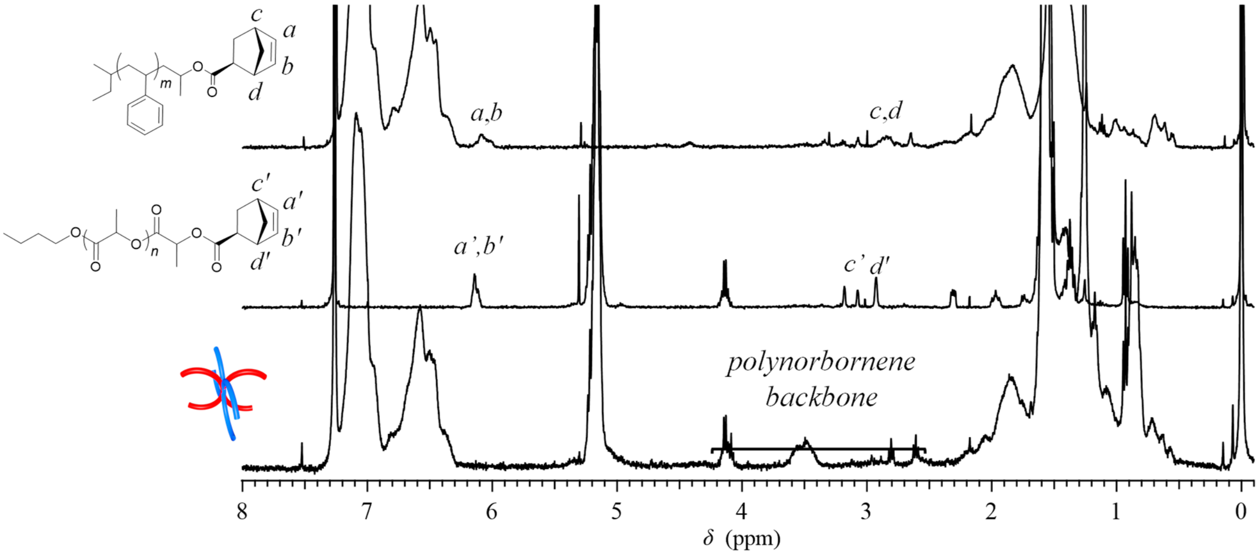


Figure S25. ^{1}H NMR spectra of PS$_{3k}$–NB (upper), PLA$_{3k}$–NB (middle), and poly(PS-*st*-PLA) (lower) in CDCl$_3$.

S4. Reference

1 T. L. Choi and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2003, **42**, 1743–1746.